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XLVIII. *Vortices behind Aerofoil Sections and Rotating Cylinders.* *By* E. TYLER, *M.Sc.*, *A.Inst.P.* (*Lecturer in Physics, College of Technology, Leicester*) *.

Introduction †.

THIS paper is supplementary to that of Richardson ‡ on "The Critical Velocity of Flow past Objects of Aerofoil Section." In his paper he confined his attention to: (1) the measurement of critical velocities of flow at which eddying motion was first produced in the wake of an aerofoil for varying angles of incidence θ with the air-stream, and his results showed a gradual drop in the Reynolds number $\frac{VD}{\nu}$ from 60 to 45 as the angle θ increased from 0 to 20°, followed by a sharper drop for increasing angles up to 30°; and (2) the relation between the non-dimensional quantities $\frac{V}{ND}$ and $\frac{VD}{\nu}$ for different values of θ ranging from 0 to 30°, where

V = velocity of the air-stream.

N = frequency of formation of the eddies.

D = maximum thickness of aerofoil.

ν = kinematical viscosity of the Fluid.

* Communicated by the Author.

† This work was carried out in the Carey Foster Laboratory, University College, London, in 1926.

‡ Proc. Phys. Soc. Lond. vol. xxxvii. April 1925.

The results cited by the author indicated that $\frac{V}{ND}$ was unaltered for increasing values of θ, and no definite empirical relation existed between the quantities $\frac{V}{ND}$ and $\frac{VD}{\nu}$, and it was from this point of view that I investigated further into the behaviour of such eddying flow behind aerofoils.

Many theoretical and experimental* results have been given with respect to fluid motion past objects of finite dimensions, and recently much attention has been given to the study of air-flow past aerofoil sections; and in all such work, provided the velocity of flow exceeds a critical value (*cf.* Reynolds's value), a turbulent region of vorticity is indicated in the wake ; but at the time of investigation I was not aware of any method having been given for the determination of the actual paths of the centres of the vortex system therein, neither any results obtained except those given by Richardson for values of $\frac{V}{ND}$ for varying values of $\frac{VD}{\nu}$ and θ.

The work contained in the present paper divides itself into two sections :—

(1) The application of Relf and Simmons's † Hot-wire method for the determination of the frequency of formation of the Benard-Kármán ‡ system of vortices behind obstacles of different sections, primarily aerofoil sections inclined at different angles of incidence to the wind-stream ; and (2) the tracing-out of the paths of the centres of the vortices formed behind stationary and rotating obstacles (*e. g.*, rotating cylinder and stationary aerofoils).

Frequency Determination of Vortices behind Aerofoils in Air.

In order to determine the frequency N of the vortices formed behind the aerofoil, the method employed was

* Piercy, Aeronautical Soc. Journ. Oct. 1923. Levy, *ibid.* June 1919 and Phil. Mag. vol. x. Oct. 1926. Howland, Aeronautical Soc. Journ. April 1925. Bairstow and Lanchester, 'Aerodynamics and Aeronautics.' Judge, 'Theory of Aerofoils.' Glauert, 'Aerofoil and Airscrew Theory.'

† Phil. Mag. vol. xlii. (1925); vol. xlix. (1925). Relf, Aeronautical Soc. Journ. April 1925.

‡ *Comptes Rendus,* cxlvii. p. 839 (1908). *Phys. Zeit.* xiii. p. 433 (1912).

essentially that first used by Relf and Simmons, and described by me in the ' Journal of Scientific Instruments ' *.

An electrically-heated platinum wire (1 inch long and ·001 inch diameter) was mounted horizontally behind the obstacle in a wind-channel $1\frac{1}{2} \times 1\frac{1}{2} \times 12$ feet, and was connected up in series with the primary of a step-up transformer (ratio 1 : 2), the secondary of which formed part of a shunted vibration galvanometer circuit. The wind-speed measured by a Chattock gauge was adjusted until resonance occurred between the frequency of formation of the vortices and the galvanometer set at known frequency, the latter being previously calibrated by means of a previously-calibrated vibrating reed.

The galvanometer frequency was also checked by stroboscoping a reflected spot of light from a mirror attached to the instrument. An Einthoven string galvanometer was substituted later for the vibration galvanometer, but this arrangement proved too insensitive. Precautions were however taken to ensure that the velocity of the air-stream V, and the frequency N of the vortices, were not too high, in order to give an appreciable drop in the resistance of the hot wire between successive periodic heatings and cooling, thereby increasing the sensitivity of the method employed, for results obtained by Richards † on the resistance of a hot wire in an alternating air-current clearly emphasized the importance of this condition being satisfied.

These conditions were met with partly in the design of the aerofoils, but care was taken that the ratio of maximum width to chord was of the same order as met with in actual practice. Different lengths of aerofoil consisting of brass and wood were used, and in most cases their length extended completely across the wind-channel and at right angles to the direction of the stream. Dimensions of sections of

TABLE I.

Section No.	Type.	Length.	D.	C.
1.....	Wooden.	37·5 cm.	·775 cm.	5·00 cm.
2.....	,,	38·0 ,,	·337 ,,	2·50 ,,
3.....	Brass.	16·0 ,,	·330 ,,	2·60 ,,
4.....	,,	20·8 ,,	·182 ,,	1·30 ,,

* Journal of Scientific Instruments, vol. iii. Sept. 1926.

† Phil. Mag. vol. xlv. May 1923.

models are shown in Table I. and fig. 1, and results for aerofoils in air are included in Tables II. and III.

Fig. 1.

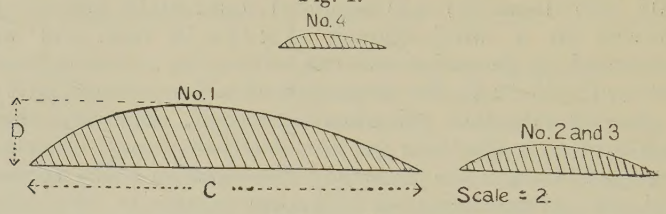


TABLE II.

Type of Aerofoil.	Angle of Incidence. $\theta°$.	D. cm.	N. per sec.	V cm./sec.	$\frac{V}{ND}$.	$\frac{VD}{\nu}$.
Wooden. No. 1. (Blunt Trailing Edge.)	−5·0	·791	15·0	80·0	6·74	$4·28\times10^2$
	−3·0	,,	15·0	92·0	7·74	4·92 ,,
	−3·0	,,	22·5	125·0	7·00	6·66 ,,
	0	,,	22·5	137·0	7·68	7·30 ,,
	5·0	,,	22·5	133·0	7·46	7·12 ,,
	6·5	,,	22·5	138·0	7·74	7·37 ,,
	8·0	,,	22·5	173·0	9·74	9·25 ,,
	8·0	,,	26·5	205·0	9·76	10·85 ,,
	10·0	,,	15·0	120·0	10·20	6·42 ,,
	*10·0	,,	22·5	175·0	9·68	9·32 ,,
Wooden. No. 1. (Sharp Trailing Edge.)	0	·775	22·5	108·0	6·22	$5·67\times10^2$
	2·5	,,	22·5	125·0	7·20	6·55 ,,
	2·5	,,	30·0	170·0	7·30	8·92 ,,
	5·0	,,	22·5	142·5	8·16	7·45 ,,
	7·5	,,	30·0	215·0	9·48	11·21 ,,
	7·5	,,	22·5	180·0	10·38	9·45 ,,
	*10·0	,,	30·0	226·0	9·94	11·84 ,,
Wooden. No. 2.	0	·337	22·5	70·0	9·20	$1·60\times10^2$
	0	,,	30·0	87·0	8·60	1·98 ,,
	0	,,	37·5	113·0	8·96	2·57 ,,
	5·0	,,	22·5	83·0	10·92	1·92 ,,
	5·0	,,	30·0	105·0	10·38	2·39 ,,
	5·0	,,	37·5	126·0	10·00	2·87 ,,
	10·0	,,	22·5	87·3	11·50	1·99 ,,
	10·0	,,	30·0	114·0	11·30	2·60 ,,
	10·0	,,	37·5	147·0	11·70	3·34 ,,
	15·0	,,	22·5	106·0	13·94	2·41 ,,
	15·0	,,	30·0	140·0	13·88	3·19 ,,
	20·0	,,	30·0	185·0	18·20	4·22 ,,
	25·0	,,	22·5	150·0	19·96	3·42 ,,

* Limit of observations.

Table IV. also shows a few results for cylinders and square section obstacles which are in good agreement with results

of previous experimenters using different methods, and a summary of the results contained in Tables II., III., and IV. is represented graphically in figs. 2 and 3.

TABLE III.

Type of Aerofoil.	Angle of Incidence. θ.	D. cm.	N. per sec.	V. cm./sec.	$\frac{V}{ND}$.	$\frac{VD}{\nu}$.
Brass. No. 1.	2·5	·182	30·0	75·0	13·74	$·92\times10^2$
	2·5	„	30·0	85·0	15·60	1·04 „
	7·5	„	30·0	87·0	16·00	1·07 „
	5·0	„	30·0	75·0	13·74	·92 „
	7·5	„	30·0	78·0	14·30	·96 „
	7·5	„	37·5	98·0	14·38	1·20 „
	9·5	„	30·0	90·0	16·50	1·11 „
	12·0	„	30·0	100·0	18·30	1·23 „
	15·5	„	30·0	106·0	19·50	1·30 „
Brass. No. 2.	0·0	·330	31·7	102·0	9·70	$2·28\times10^2$
	0·0	„	27·5	95·0	10·40	2·11 „
	6·0	„	29·5	105·0	10·78	2·34 „
	7·0	„	25·0	106·0	12·84	2·36 „
	10·0	„	29·5	125·0	12·88	2·78 „
	10·0	„	36·5	211·0	14·26	4·71 „
	11·0	„	27·5	143·0	15·70	3·19 „
	15·0	„	25·0	156·0	18·92	3·48 „
	15·0	„	15·0	135·0	18·20	3·01 „
	30·0	„	29·5	150·0	(15·40)	3·35 „

TABLE IV.

Obstacle.	D. cm.	N. per sec.	V. cm./sec.	$\frac{V}{ND}$.	$\frac{VD}{\nu}$.
Cylinder.	2·0	34·0	360·0	5·29	$4·87\times10^3$
	—	30·0	322·0	5·36	4·37 „
	—	28·5	302·0	5·26	4·10 „
	—	14·25	146·0	5·12	1·98 „
	*2·0	1·0	10·50	5·20	$1·42\times10^2$
Square Cords.					
Wooden.	1·30	15·0	213·0	10·94	$1·87\times10^3$
	1·30	14·75	246·5	13·30	2·17 „
	·65	14·75	100·0	11·46	$4·40\times10^2$
	·615	15·0	103·0	11·20	4·28 „
	·615	22·5	155·0	11·20	6·49 „
	·615	30·0	201·0	10·94	8·35 „
Rubber.	·265	30·0	85·0	10·70	$1·52\times10^2$
	·250	30·0	85·0	11·30	1·43 „
	·250	37·5	115·0	12·30	1·94 „
	*·340	146·0	580·0	11·70	$1·33\times10^3$

* Richardson's results.

Fig. 2.

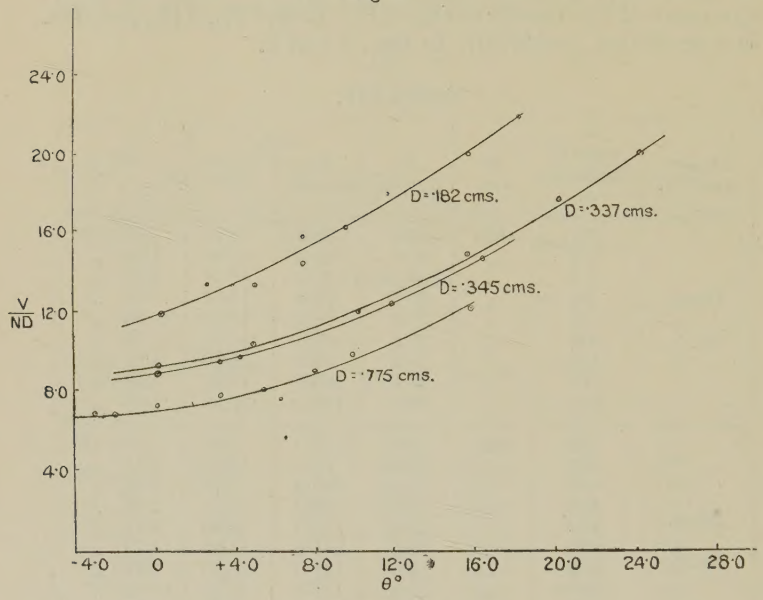
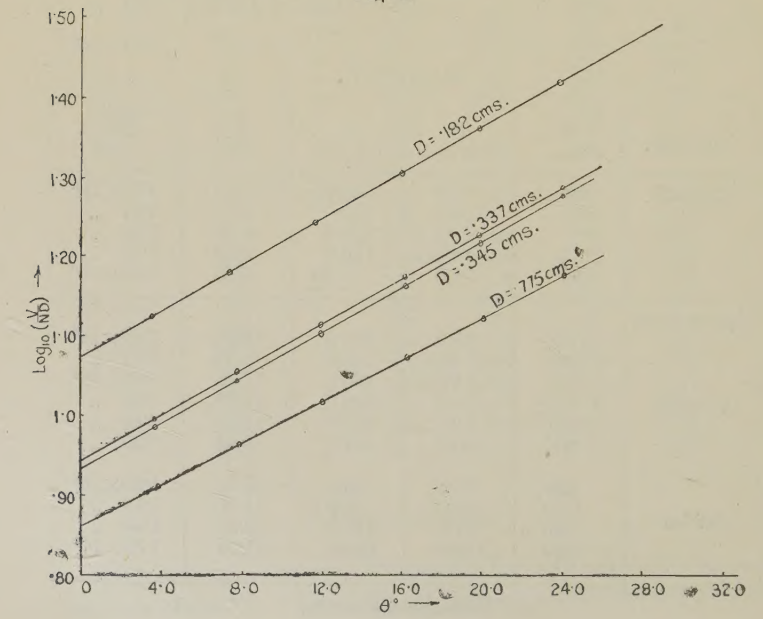

24·0
20·0
16·0
12·0
8·0
4·0
V/ND
D=·182 cms.
D=·337 cms.
D=·345 cms.
D=·775 cms.
-4·0
0
+4·0
8·0
12·0
16·0
20·0
24·0
28·0
θ°

Fig. 3.

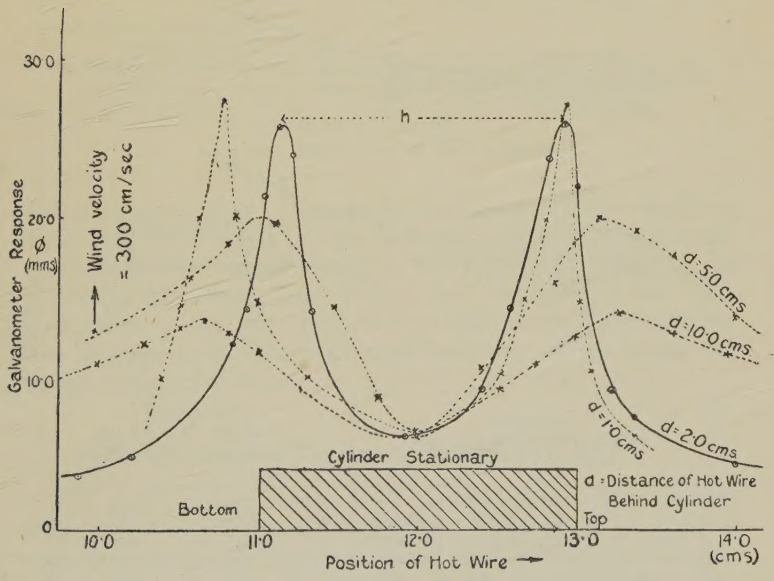

1·50
1·40
1·30
1·20
1·10
1·0
·90
·80
Log10 (V/ND)
D=·182 cms.
D=·337 cms.
D=·345 cms.
D=·775 cms.
0
4·0
8·0
12·0
16·0
20·0
24·0
28·0
32·0
θ°

Determination of the Paths of Vortices.

The wind-speed having been adjusted until resonance occurred between the frequency of formation of the vortices and the galvanometer set at a known frequency, the deflexion ϕ of the galvanometer was assumed proportional to the amount of periodic cooling of the hot wire.

The wire was then traversed in a vertical plane and at distances d behind the obstacle and corresponding deflexions ϕ observed. Typical results for a stationary cylinder are shown in fig. 4, the curves each showing two maxima, and

Fig. 4.



the distance between such was taken as a measure of the separation distance h between the two rows of alternate vortices, since the maximum amount of periodic cooling occurs along the paths of the centres of the vortices.

The variations of h with d, both for a cylinder and inclined aerofoil (wooden) at 0°, 5°, and 8° to the stream, are shown in fig. 5, and the results are shown in Table V.

A limit to the observations for this aerofoil was reached at an angle between $8° \sim 10°$, for on increasing the angle of incidence beyond this value the motion of the air in the wake

of the aerofoil exhibited a general turbulent motion; and no definite resonance frequency was found.

Fig. 5.

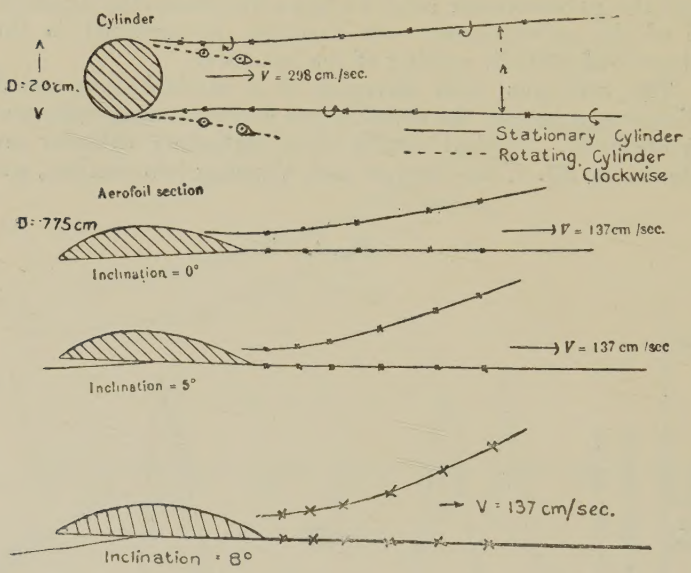


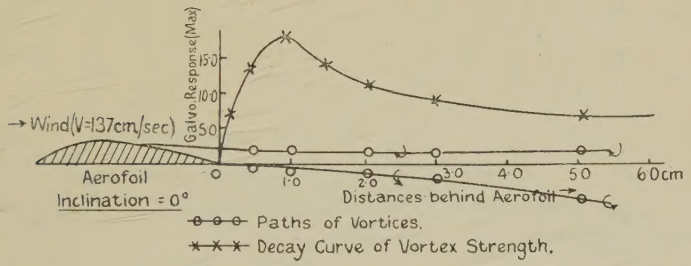
TABLE V.

Aerofoils. Wind-speed = 137 cm./sec.				Stationary. Cylinder D = 2·0 cm. Wind-speed = 298 cm./sec.	
d. cm.	$\theta=0°$. *h* (cm.).	$\theta=5°$. *h* (cm.).	$\theta=8°$. *h* (cm.).	*d.* cm.	*h.* cm.
·10	·60	·67	·70	·50	2·30
·50	·50	·56	·86	1·00	2·10
1·0	·45	·52	·90	2·0	1·80
1·50	·70	·80	1·0	5·0	2·15
3·00	1·00	1·10	1·15	7·0	2·41
5·00	1·20	1·30	1·55	10·0	2·60

This condition was no doubt due to the sudden change in the ratio of lift to drag at this inclination, which is characteristic of aerofoils in general. With other aerofoils used, it was found, however, possible to extend the results to higher values of θ (*vide* Tables II., III., and IV.).

The maximum response of the vibration galvanometer (previously tuned to resonance frequency with the vortices) is shown clearly in fig. 6, for different positions of hot wire behind the aerofoil. The curve shows the growth and decay of a vortex as it leaves the aerofoil, and the merit of such a result is entirely dependent on keeping the heating current constant. Notice that it takes some time before the vortex reaches its maximum strength, and then it seems to

Fig. 6.



decay exponentially. It must be remembered that in working with such small-scale models there is a limit to such investigations, for the vortex strengths are small and, owing to the widening-out effect, soon decay after travelling a few cms. along their paths, and the hot-wire detector becomes insensitive to these small fluctuations of velocity, which is masked by general turbulence.

Results for a Rotating Cylinder in Air.

The above method was used to investigate the Magnus Effect * for a cylinder (D = 2·0 cm.) rotating in air, which, according to Prandtl †, results in vortices of unequal strengths being detached from the opposite sides of the cylinder when rotating. The effect is clearly shown in figs. 7, 8, and 9, which give results for different speeds of rotation of the cylinder, the curves clearly showing a lateral displacement and unequal maxima. The time at my disposal did not enable me to investigate this effect to any considerable extent, but the graphs do show the position of the vortex centres for different distances behind the rotating cylinder,

* Poggen, *Ann. d. Phys.* 1853.

† *Die Naturwissenschaften*, Feb. 6, 1925. Low, Aero. Soc. Journ. Feb. and March 1925.

Fig. 7.

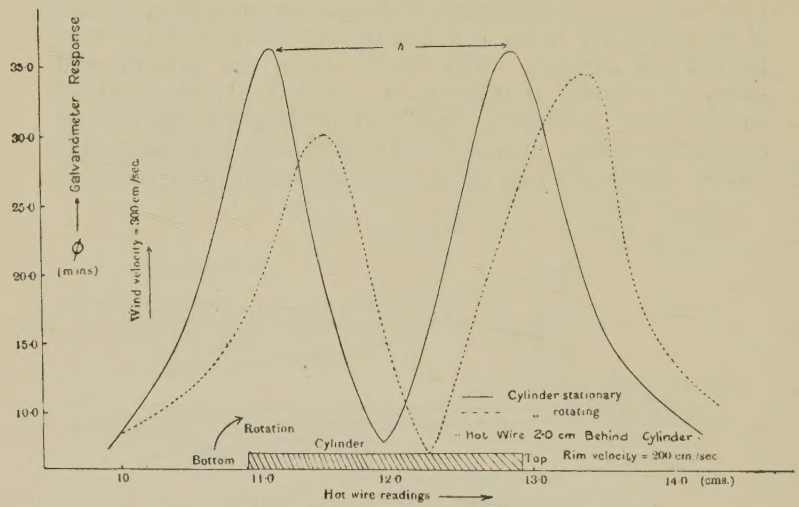
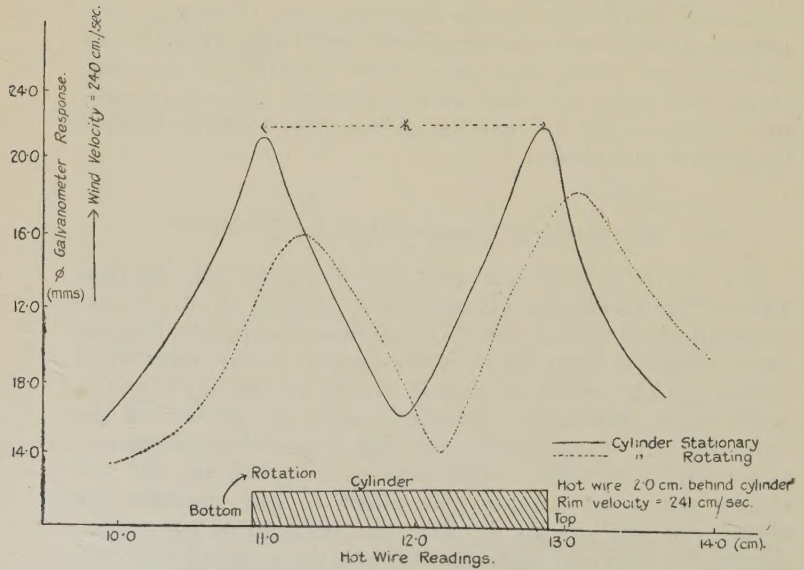


Fig. 8.



and the work could no doubt be extended to trace out the paths more completely for rotating bodies such as a cylinder, as used in this case.

Fig. 9.

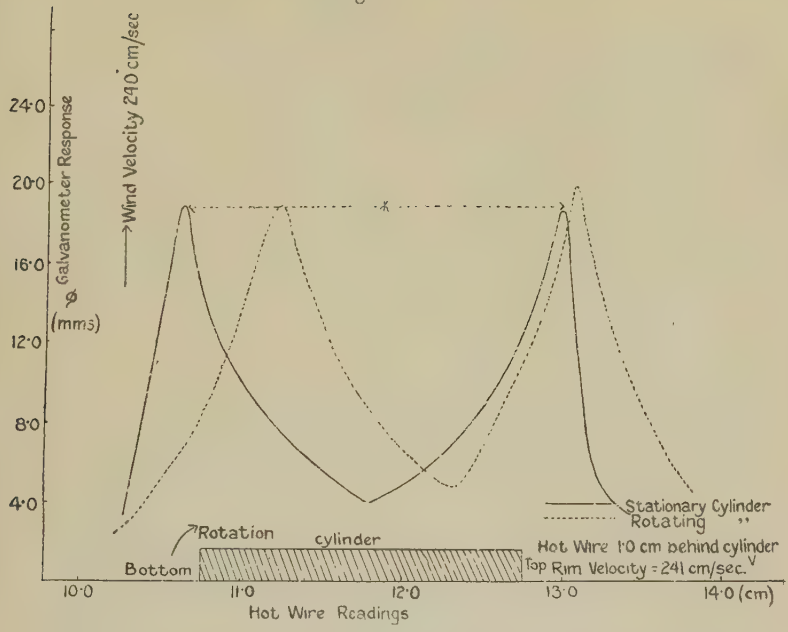


TABLE VI.*

D. cm.	θ°.	$\frac{V}{ND}$.	$\frac{V}{ND} \cdot e^{-\cdot 0323\theta} = A.$
·182	0	12·0	12·0
	4	13·7	12·3
	8	15·7	12·3
	12	17·8	12·2
	16	20·2	12·2
	20	23·0	12·2
·337	0	8·8	8·8
	4	10·0	8·9
	8	11·7	9·1
	12	13·2	9·0
	16	15·1	9·1
	20	17·2	9·3
	24	19·5	(10·0)
	28	22·0	8·9
·775	0	7·50	7·5
	4	8·0	7·1
	8	9·00	7·0
	12	10 30	7·0
	16	12·00	7·2

* Values of θ and $\frac{V}{ND}$ were interpolated from graph (fig. 2).

Theory and Discussion of Results.

(1) *Relation between* $\frac{V}{ND}$, $\frac{VD}{\nu}$, *and* θ.—The variation of these non-dimensional quantities with variation of θ shows that $\frac{V}{ND}$ increased with θ. There does not seem to be any dynamical similarity existing between the quantities $\frac{V}{ND}$ and $\frac{VD}{\nu}$ following Rayleigh's treatment, but the following empirical formula was found to fit the results approximately for $\frac{V}{ND}$ and θ, viz. :—

$$\frac{V}{ND} = Ae^{\cdot 0323\theta},$$

where A is a constant for any given aerofoil and is numerically equal to the value of $\frac{V}{ND}$ when $\theta = 0$. It should, however, be observed that A varies for different aerofoils (*vide* Table VI.).

The results of Richardson indicated no definite empirical relation existing, but his results were of the same order as mine, although obtained by a different method.

Results for square-section chords and rods (*vide* Table IV.) do compare favourably.

Benard *, working with square plates, has obtained the following relation for his results :—

$$N = \frac{\cdot 430(V - 166\nu)}{D + \cdot 307} \text{ in C.G.S. units,}$$

where N = frequency of the vortices,
V = velocity of plate relative to the liquid,
D = thickness of plate normal to stream direction,
ν = kinematic viscosity of the liquid.

His results again show no strict dynamical similarity, even with square-section obstacles, and it may be doubted whether in actual experience any simple relation is applicable to the results. The method employed is not, however, delicate enough to investigate the point at which the vortex layer leaves the surface, where such a layer on leaving the surface of the body provides the mechanism which gives rise to the Benard-Kármán system of vortices. The position of this

* *Comptes Rendus*, vol. clxxxii. June 23, 1926.

point no doubt determines in the main the drag upon the body which controls the value of $\frac{V}{ND}$.

For large values of $\frac{VD}{\nu}$ the position of this point (*vide* Lock *) is unaffected, while for small values this point may vary appreciably, and hence corresponding changes in $\frac{V}{ND}$. The upper limit of $\frac{VD}{\nu}$ where the sudden shifting back of this point causes a change in $\frac{V}{ND}$ was not reached in the experiments with the aerofoils.

(2) *Path of Vortices behind Obstacles.*

The paths traced out by the vortex centres behind a stationary cylinder show that in actual practice Kármán's theoretical results for the condition of maximum stability of vortices in two parallel rows behind an obstacle is not strictly applicable, but must be modified to meet the case of the widening-out of the rows as indicated in the results.

He has shown that if $h =$ distance between the rows and $l =$ distance between successive vortices in the same row, the condition for maximum stability is given by

$$\cosh \frac{2\pi h}{l} = 2$$

and

$$u = \frac{K}{2l} \tanh \frac{\pi h}{l},$$

where u = the translational velocity of the vortices relative to the stream and K the vortex strength, these relations giving $\frac{h}{l} = \cdot 283$.

Levy † has subsequently shown that no such system is completely stable.

This widening-out effect may be due to interference by the walls of the chamber, or may be due in the main to viscosity. Similar results have been obtained photographically by Föppl ‡, whose results were confirmed mathematically by Levy. Moreover, Kármán and Rubach § have also obtained, photographically, results of vortices in liquids, and

* Phil. Mag. Nov. 1925.
† Proc. Roy. Soc. Edin. xxxv. p. 95 (1914).
‡ *Münchene Sitzungsberichte*, 1923.
§ *Loc. cit.* ref. p. 450, and 'Aerodynamics,' by Fuch and Hopf, p. 170.

they also show this slight divergence of the rows. An analogous behaviour was observed by Richardson and myself in a recent paper * on eddy flow from annular nozzles, and Benton † has also shown that in tracing out the boundaries of the eddy tracks in the case of a straight slit and wedge over a considerable range, we get a widening of the eddy paths. Fage and Johansen ‡ have also shown that there is a widening-out of the paths for vortices behind an inclined plate as the vortices recede from the plate.

Referring to fig. 5, it will be seen that the paths behind the given aerofoil also indicate a gradual widening as the vortices recede from the aerofoil ; but as the inclination is increased, the vortices tend to widen out more rapidly, and there is a limit to the observations that can be made, owing to the insensitiveness of the method used.

Piercy §, using a Pitot-tube method, has obtained a few similar results, but the work of Bryant and Williams, Fage, Simmons and Taylor ‖, who show regions of vorticity in the wake of an aerofoil, is well supported by my results. Bjerknes's¶ idea of only one vortex being detached from the tip of the aerofoil, which leaves it with the stream while the next alternate one circulates round the aerofoil, thereby contributing to the circulation, is evidently not supported by my results, for they point to two vortices being detached, say, alternately one from the tip of the aerofoil and one from the upper surface, both practically of equal strength (in so far as the apparatus is able to detect), for the maxima of the resonance curves on either side of the section were equal, though relatively closer than for a cylinder.

According to Prandtl's theory, he supports Bjerknes's idea, but this condition I have failed to detect if it exist. The results suggest the vortices are in the main due to ordinary "æolian tone" phenomena, the effective thickness D of an aerofoil being modified as its angle of inclination to wind-stream is varied ; and since the stagnation points are symmetrically placed with respect to the trailing edge, yet at different distances along the boundary from the leading edge, these conditions tend to maintain equal vorticity on both sides.

In the case of the rotating cylinder, whereas there is no

* Phil. Mag. vol. ii. Aug. 1926.
† Proc. Phys. Soc. vol. xxxviii. p. 114 (1926).
‡ Proc. Roy. Soc. vol. A, p. 116 (1927).
§ *Loc. cit.* ref. p. 450.
‖ Phil. Trans. A, p. 630, Nov. 1925 ; p. 632, Dec. 1925.
¶ *Journal de Physique,* 1924.

change in the frequency of the vortex formation for a rotating as compared with a stationary cylinder, there are vortices of unequal strengths formed, each displaced laterally from its original path.

Relf and Lavender *, photographing the flow round a rotating cylinder, conclude from their results that the total vorticity is less for a rotating cylinder than for a stationary cylinder, thus accounting for a reduction in the drag. I have failed to detect any change in the value of $\frac{V}{ND}$ which may occur owing to this reduction, but it may be noted that the peaks of the curves (figs. 8 and 9) for a rotating cylinder—cases in which the vortex has had time to reach its maximum strength—do indicate smaller values than when the cylinder is stationary.

A similar phenomena has been observed by Befort †, using spinning disks in an air-stream, and also by MM. Turpain and Bouy de Lavergne ‡. Photographs by Bairstow § also confirm this, but recently Tietjens ‖ claims to have detected the formation of vortices on one side only of a rotating cylinder, and he supports his results by photographs, a result which would favour Bjerknes's theory for the aerofoil; but it is to be doubted whether such evidence will lead to any simple theory.

It is hoped, however, that the results given herewith, although entirely experimental, will provide data for further suggestions in aeronautical research.

In conclusion, I wish to express my best thanks to my colleague, Dr. E. G. Richardson, who suggested to me this line of research as an extension of his earlier investigations, and also to Professor A. W. Porter, F.R.S., for his kindly interest taken and also for putting the facilities at my disposal during the course of this research.

* Adv. Committee of Aeronautics, No. 1010 (1925).
† *Zeits. f. Phys.* vol. xxxvi. 5, p. 374 (1926).
‡ *Comptes Rendus*, vol. clxxxii. April 1926.
§ 'Nature,' March 28, 1925.
‖ *J. de Wiss. Geo. f. Luftfahrt*, vol. xviii. p. 56 (1925).

XLIX. *Contribution to the Theory of Photographic Exposure.* *By* L. Silberstein, *Ph.D.* (Communication No. 336.)*

Difficulties of the Quantum Theory.

THE quantum or light-dart theory of photographic exposure, as formulated and developed in my previous papers †, recommended itself by its essential simplicity and some other encouraging features, while the underlying concept of the propagation and incidence of light in discrete energy parcels, Einstein's light-quanta, was not a hypothesis introduced *ad hoc*, but one that had already scored notable successes in other fields. That theory represented, roughly at least, the observed facts, and the discrepancies between the theoretical results and the experimental findings, viz., the number of grains of a given size made developable by a given exposure, have at that time seemed rather irregular and not seriously exceeding the limits of experimental error. But after a more detailed scrutiny, the deviations of the theory from experiment turned out to be distinctly systematic, and Dr. Toy's criticism ‡ of 1923 was more recently found by Sheppard, Trivelli, and Loveland § to be materially correct. No great weight, perhaps, can be given to Toy's results and criticism concerning the dependence of the number of affected grains on wave-length. But the dependence of that number on exposure and grain size (area), as shown by Toy's own data, and especially by a set of results obtained in this laboratory with the Slow Process emulsion, is certainly not well represented by the formulæ of the quantum theory. Some minor discrepancies may perhaps be disregarded. But what in the writer's own opinion seems particularly unsatisfactory about the formulæ yielded by that theory is the following feature.

Both the original formula ‖,

$$k = N(1 - e^{-na}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

as well as the modified one,

$$k = N(1 - e^{-n\epsilon a}), \text{ with } \epsilon = \text{const.}, \quad . \quad (b)$$

* Communicated by the Author. From the Kodak Research Laboratories.

† Phil. Mag. vol. xliv. pp. 257 & 956 (1922); vol. xlv. p. 1062 (1923).

‡ Phil. Mag. vol. xlv. p. 715.

§ Journal Franklin Inst. July 1925, p. 51.

‖ There N is the total number of silver halide grains, k that made developable, a the size (area) of a grain, and n the number of light-quanta incident per unit area.

make k grow at first proportionally to n, *i.e.*, to the exposure itself, and then still slower, while experimentally k was found to increase (after the very first short stage of slow linear growth) as rapidly as and even more rapidly than the square of the exposure. This state of things is not much changed when formula (b) is replaced by the somewhat more refined equation

$$\frac{k}{N} = 1 - e^{\bar{\kappa}(e^{-n\omega}-1)}, \quad . \quad . \quad . \quad . \quad . \quad (c)$$

obtained (III. paper, *loc. cit.* p. 1066) by splitting the sensitive fraction ϵa of the area of each grain into a number of separate sensitive "spots," each of area ω, distributed haphazardly among the grains, $\bar{\kappa}$ being the average number of such spots per grain. In fact, this modification not only does not increase the rate of growth of k, but rather reduces it somewhat. Similarly as for (b), the gradient dk/dn corresponding to formula (c) decreases always with increasing n from its initial value $N\omega\bar{\kappa}$ down to zero for $n=\infty$. In fact, the second derivative is, by (c),

$$\frac{d^2k}{dn^2} = -\frac{\bar{\kappa}\omega}{N} e^{-\omega n}[1+\omega(N-k)], \quad . \quad . \quad . \quad (c'')$$

and thus throughout negative. In fine, the corresponding k, n curve has no inflexion point, while there is a distinct indication of such a point in the experimental curves.

To meet this difficulty, two more modifications of the light-dart theory were tried.

The first of these consisted in assuming that a silver halide grain is made developable when it is hit (within its sensitive part ϵa) not by a single light-dart, but by at least *two*, or at least *three*, generally by at least r darts. The formula corresponding to this assumption is easily found to be *, for $r=2$,

$$\frac{k}{N} = 1 - e^{-\epsilon an}(1+\epsilon an), \quad . \quad . \quad . \quad . \quad (d_2)$$

and generally, for any r,

$$\frac{k}{N} = 1 - e^{-\epsilon an}\left[1 + \frac{\epsilon an}{1!} + \frac{(\epsilon an)^2}{2!} + \ldots + \frac{(\epsilon an)^{r-1}}{(r-1)!}\right]. \quad (d_r)$$

Now, each of these k, n curves has an inflexion point, namely at $\epsilon an = r-1$. Thus, for example, the curve (d_2)

* It is enough to remember that, if $\bar{\kappa}$ be the average number of darts per grain (within the sensitive part of its area), the probability that the sensitive area of a grain shall be hit by s darts is $e^{-\bar{\kappa}}\bar{\kappa}^s/S!$, and that in the present case $\bar{\kappa}=\epsilon an$.

has its inflexion point at

$$\epsilon an=1, \quad \frac{k}{N}=0{\cdot}264$$

(*i. e.*, where 26 per cent. of the grains are made developable), and it actually approaches the experimental curves belonging to the Slow Process emulsion* within a certain interval somewhat more closely than did the original curve ($r=1$), yet without representing any of these curves accurately enough. The ordinate of the inflexion point of (d^2) being already somewhat too great, the curves (d_r) corresponding to $r=3$, 4, etc., have their inflexion points placed still higher, at $\frac{k}{N}=0{\cdot}32$, $0{\cdot}35$, etc., and thus much above the more or less distinct indications of the experimental inflexion points. Accordingly, none of these theoretical curves can be expected to give a satisfactory representation of the experimental results, and they may be left on one side.

In the second modification it was assumed that, even for equal grains, the sensitive fraction ϵ of their area differs from grain to grain, the form of the frequency distribution law of the ϵ-values among the grains being left entirely free. Thus, let the number of grains, whose sensitivity factor lies between ϵ and $\epsilon+d\epsilon$, be given by

$$Nf(\epsilon)d\epsilon,$$

where f is an arbitrary (but of course positive) function of ϵ and N the total number of grains. Then, by the original, single-hit assumption of the quantum theory of exposure, and noticing that the whole range of ϵ extends from 0 to 1, the number of grains affected by an exposure n will be

$$k=N\int_0^1 f(\epsilon)\left[1-e^{-na\epsilon}\right]d\epsilon,$$

and remembering that

$$\int_0^1 f(\epsilon)d\epsilon=1,$$

$$\frac{k}{N}=1-\int_0^1 f(\epsilon)e^{-na\epsilon}d\epsilon. \quad . \ . \ . \ . \ (e)$$

Now, developing the exponential function into a power series, this formula can be written

$$\frac{k}{N}=na\int_0^1 \epsilon f(\epsilon)d\epsilon-\frac{n^2a^2}{2!}\int_0^1 \epsilon^2 f(\epsilon)d\epsilon+\frac{n^3a^3}{3!}\int_0^1 \epsilon^3 f(\epsilon)d\epsilon-\ldots$$

$$. \ . \ . \ (e')$$

* These data will be quoted below.

This series is convergent for every value of na. For so is the series

$$na - \frac{n^2a^2}{2!} + \frac{n^3a^3}{3!} - \cdots,$$

and, since

$$\int_0^1 f(\epsilon)d\epsilon = 1,$$

all the coefficients

$$\int_0^1 \epsilon^\kappa f(\epsilon)d\epsilon$$

are smaller than unity. For small values of na (which is a pure number) the number k of grains affected will be proportional to n or to the exposure, regardless of the form of the function f. If this initial proportionality of k to n is to pass into a more rapid increase of k, to be necessarily followed again by a slower one (since ultimately the rate of increase tends to zero), the corresponding curve must have an inflexion point, or d^2k/dn^2 must be zero for a certain value of n. Now, by (e),

$$\frac{d^2k}{dn^2} = -Na^2\int_0^1 \epsilon^2 f(\epsilon)e^{-\epsilon an}d\epsilon,$$

and since the integrand is always positive, d^2k/dn^2 cannot vanish for any finite value of n. In other words, the gradient dk/dn of the curve always decreases, from $n=0$ to $n=\infty$. There is thus no possible form of the distribution function $f(\epsilon)$ which would give a faithful representation of the experimental findings.

Nuclear Theories.

The possibilities of the quantum theory of photographic exposure being thus completely exhausted, it has seemed worth while to investigate the implications of theories which are based upon essentially different assumptions and concepts, and which may summarily be referred to as *nuclear* theories of exposure. In these theories the chance factor which we have thrown upon the impinging light, making the developability of a grain of silver halide depend upon the chance of its being hit by one or more light-darts, is transferred upon the grains themselves, which are assumed to contain, before the exposure, certain heterogeneities, specks of a foreign substance * accompanied by some free silver atoms, or incipient nuclei haphazardly distributed among them with

* Notably silver sulphide (Sheppard).

respect to number as well as to size. The part played by the incident light (whose possibly discrete structure becomes irrelevant) consists, then, in maturing or completing these nuclei by depositing upon and around them further free silver atoms, and thus increasing them until they become "active" (*i. e.* developable), while every grain containing at least one active nucleus is assumed to be developable as a whole. The latter property can actually be considered as an experimentally established fact.

The concept of nuclei, which could be traced back a long way, has been utilized in a theory proposed in 1922 by F. C. Toy * and more recently (1925), and in a modified form in a theory outlined by Sheppard, Trivelli, and Loveland (*loc. cit.*), who refer to it as the "concentration speck" theory. The former is of a semi-quantitative nature, Dr. Toy's assumptions not being given by him a definite mathematical form, while the latter is mainly qualitative, and leaves therefore its quantitative development free within wide limits.

In what follows, our purpose is, first, to put Toy's theory into a definite mathematical form, and, second, to substantiate some of the possible interpretations of the concentration speck theory or, rather, to develop the consequences of assumptions which were suggested by this theory.

Mathematical Formulation of Toy's Theory.

According to Toy's assumption, there are, previous to exposure, a certain number of nuclei distributed haphazardly among the grains. These nuclei are supposed to differ in "sensitivity," *i.e.* to require different light-intensities I (at constant exposure time), or ultimately † different (energy-) exposures E in order to become active nuclei or development centres. Of the curve which is to represent the distribution of the nuclei over the E-range (or, in his own case, the I-range), Toy assumes only in a qualitative way that it will be "similar in general form to that obtained by Maxwell for the distribution of the velocities between the molecules of a gas," without committing himself to any definite mathematical formula. The curve drawn in Toy's fig. 1 (*loc. cit.*) resembles Maxwell's frequency-distribution curve for *resultant* velocities (regardless of direction), which would be expressed by

$$f(v)dv = \text{const. } e^{-hv^2}v^2dv,$$

and thus passes through the origin, $v=0$. But there is

* Phil. Mag. vol. xliv. p. 352.

† Apart from the failure of the reciprocity law.

manifestly no reason for supposing the (reciprocal) "sensitivities," *i. e.* the E-values, to be thus distributed among the nuclei. The case in hand can rather be expected to be ruled by Maxwell's distribution law for each of the three rectangular *components* of velocity, which is simply the normal frequency-distribution law. A factor E^2 corresponding to v^2, which in the case of the molecules is due to replacing the volume-element of the velocity-space $dv_x\,dv_y\,dv_z$ by $v^2 \sin\theta\,d\theta\,d\phi\,dv$ and which remains in the formula after an integration over all directions (θ, ϕ) in that space, has no justification whatever in the case of the nuclei, whereas it is reasonable to assume for these the normal distribution law.

Let us therefore definitely assume that the number of nuclei requiring an exposure E to $E+dE$ in order to become active nuclei is

$$f(E)dE - Ae^{-h^2(E-E_0)^2}dE, \quad . \quad . \quad . \quad . \quad (1)$$

where A, h, and E_0 are constants. Then the number of *active nuclei*, $N\kappa_a$ say, produced by an exposure E will be

$$N\kappa_a = A\int_0^E e^{-h^2(E-E_0)^2}dE,$$

or, in terms of the error-function

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2}du,$$

$$N\kappa_a - C\{\Phi[h(E-E_0)] + \Phi(hE_0)\}, \quad . \quad . \quad . \quad (2)$$

where C is a constant proportional to A/h. Let $N\kappa$ be the total number of nuclei. This will be given by (2) for $E=\infty$.

Thus, and since $\Phi(\infty)=1$,

$$N\kappa = C\{1+\Phi(hE_0)\}, \quad . \quad . \quad . \quad . \quad (2')$$

which determines the constant C. Since N is the number of grains, κ is the average number of all nuclei, and κ_a the average number of active nuclei per grain.

Thus, by (2) and (2′), the average number of active nuclei per grain produced by an exposure E will be

$$\kappa_a = \kappa\frac{\Phi[h(E-E_0)] + \Phi(hE_0)}{1+\Phi(hE_0)}. \quad . \quad . \quad . \quad (3)$$

Let us now assume, after Toy, that every grain which happens to have one or more active nuclei will be developable. This, at any rate, is a safe assumption; for, as already mentioned, it is only a re-statement of the well-established fact that a grain which once starts developing will be developable entirely.

Now, since the $N\kappa_a$ active nuclei can be supposed to be haphazardly distributed among the grains, the probability of a grain having none of these nuclei is $e^{-\kappa_a}$. The number of grains, out of the large total N, having no active nucleus will be $Ne^{-\kappa_a}$, and the number of grains having at least one active nucleus, and therefore, by the last assumption, the number of grains made developable,

$$k = N(1-e^{-\kappa_a}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we put for brevity

$$v \equiv \log \frac{N}{N-k},$$

this result can be written

$$v = \kappa_a. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Thus, ultimately, by (3),

$$v = \kappa \frac{\Phi[h(E-E_0)] + \Phi(hE_0)}{1+\Phi(hE_0)} \quad . \quad . \quad . \quad . \quad (5)$$

Such, then, would be the relation between v and the exposure E as a consequence of assuming (1) as the distribution law of sensitivity. The equation (4 *a*) itself, is, of course, independent of any such law, its validity being based only on the assumption that the active nuclei are distributed haphazardly among the grains.

Now, while the equality $v = \kappa_a$ seems to hold accurately enough, in Toy's two sets of data *, at least, the curve (5) does not resemble very much that sketched in his fig. 2, and certainly does not represent well enough either his own observed v-values or those found by Trivelli for the Slow Process emulsion. The curve (5) has an inflexion point, namely at $E = E_0$, but it differs considerably in shape from the experimental curves. To see this, it is enough to take a few numerical examples of equation (5), which, with $y = v/\kappa$ and $x = hE$, can be written

$$y = \frac{\Phi(x-x_0)+\Phi(x_0)}{1+\Phi(x_0)}, \quad . \quad . \quad . \quad . \quad (5')$$

* These two sets are contained in Toy's Table II. (*loc. cit.* p. 361). Assuming that the grains which show no nuclei would not develop at all, we find from the first set

$$N-k=91,\ v=\log\frac{150}{91}=0{\cdot}50, \text{ as against } \kappa_a=0{\cdot}48 \text{ (Toy's } N_0),$$

and from the second set

$$v=\log\frac{150}{45}=1{\cdot}25, \text{ while } \kappa_a=1{\cdot}19.$$

x_0, the abscissa of the inflexion point, being its only parameter.

Thus for $x_0 = 0{\cdot}20$ we have

x ..	0·05	0·10	*0·20*	**·30**	·40	·60	·80	1·20	1·60	2·50
y ...	0 045	0 090	0·182	·274	·364	·533	·676	·872	·961	·999.

This curve is up to about $y = 0{\cdot}50$ scarcely distinguishable from a straight line through the origin, y being almost proportional to x. The behaviour of the curve (5) is very much the same for other values of x_0. Since the experimental inflexion point lies, at any rate, in the lower part of the x-scale (and the extreme, asymptotic value of y is 1), it is enough to consider such values of x_0 for which $2y_0$ does not approach unity. Thus, on the one hand, for $x_0 = 0$, y becomes equal to $\Phi(x)$ itself, which from zero up to about $y = 0{\cdot}40$ is very nearly proportional to x, as may be seen from a table of the error-function. On the other hand, for $x_0 = 0{\cdot}75$, which places y_0 already too high, pairs of corresponding values are

x	$\frac{1}{8}x_0$	$\frac{1}{4}x_0$	$\frac{1}{2}x_0$	x_0	$2x_0$	$4x_0$
y	0·038	·080	·179	·416	·831	$·999_3$

Even here y increases, but slightly more rapidly than x.

Now, the relation between v and exposure as found experimentally is of a distinctly different type, especially for the smaller grains. Thus, in Toy's experiments (*loc. cit.* Table IV.), when for the smallest grains, class (a), the exposure is nearly doubled (61 : 128), the value of v increases from ·05 to ·62, more than tenfold, and in the next size class, on doubling the exposure, the value of v is more than trebled, and so on. The disagreement with (5) is still more pronounced in the case of Trivelli's results for the Slow Process emulsion. In fact, for the smallest grains ($a = 0{\cdot}115\mu^2$) the observed v-values, for exposures E increasing in the ratio $1 : \sqrt{2}$, are

0·026 0·11 0·36 0·74 1·29, etc.,

i. e. increasing much more rapidly than E, and for the next size class ($0{\cdot}3\mu^2$)

0·14 0·21 0·37 0·72 1·44 2·13, etc.,

still increasing more rapidly than E.

Notice that while by (5) v should tend with indefinitely increasing exposure to a *finite limit* $v_\infty = \kappa =$ average number of all nuclei per grain, it is difficult to tell whether the experimental results, either Toy's or Trivelli's, give an indication of the existence of such a limit at all. It is, at any rate, impossible to derive from these data anything but a very

rough value of this limit. (In Trivelli's case, in which v-values as high as 6 are quoted, one would as well be justified in taking $v=\infty$, since experimentally $k/N=0{\cdot}99$ to which corresponds $v=4{\cdot}6$ is just distinguishable, and $k/N=0{\cdot}999$ is scarcely discernible at all from unity to which corresponds $v=\infty$). We may only, in the case of Toy's size class (a), take provisionally for $v_\infty=\kappa$ a value just above 2·45, the highest v observed, and for the inflexion point, from Toy's smoothed curve (a) in his fig. 10, the value $v_0\doteq 0{\cdot}50$, corresponding to I or $E\doteq 0{\cdot}12$, and in this way determine $x_0=hE_0$ and compare the v-values given by (5) with the observed ones. Thus, assuming

$$v_\infty=\kappa=2{\cdot}55, \quad v_0=0{\cdot}50, \quad E_0=0{\cdot}12,$$

we have, from

$$\frac{\Phi(x_0)}{1+\Phi(x_0)}=\frac{v_0}{\kappa},$$

$$\Phi(x_0)=\frac{v_0}{\kappa-v_0}=0{\cdot}244, \text{ whence } x_0=0{\cdot}220,\ h=1{\cdot}83;$$

so that formula (5) becomes

$$v=2{\cdot}05\{\Phi(1{\cdot}83E-0{\cdot}22)+0{\cdot}24\},$$

and this gives, with E written for Toy's I in his arbitrary units,

E	1	0·689	·490	·270	·128	·061	·033	·016	·008
$v_{calc.}$	2·50	2·26	1·86	1·12	0·58	·25	·14	·06	·03

against

$v_{obs.}$	2·45	2·30	2·04	1·39	0·62	·05	·00	·00	·00

There is a marked disagreement between the calculated and the observed v-values ; the deviations increase with decreasing exposure down to the fourth and reappear in the sixth step, to become henceforth systematic. This result cannot be improved by changing the value of κ, which would only change all v-values in the same ratio. Nor can v_0, E_0 be changed appreciably without clashing with the position of the inflexion point in Toy's smoothed curve (a). Thus, Toy's set (a) of data cannot be satisfactorily represented by formula (5). The deviations in the case of Trivelli's data for the Slow Process emulsion (quoted below), especially for the first two size-classes of grains, have turned out to be even more pronounced, while Toy's remaining sets, (b), (c), (d), and the corresponding smoothed curves, for which the values

of v_0, E_0, and especially κ cannot be estimated at all, would lead to no relevant results.

In fine, the available experimental data cannot be adequately represented by the formula (5), which was arrived at by giving a definite mathematical form to Toy's assumptions. A weak point of this type of formula is, moreover, the presence of the factor κ, whose numerical determination, through v, is essentially elusive.

Such being the case, some alternative forms of nuclear theory of exposure were next considered in which the growth of the nuclei was explicitly taken into account. These forms were suggested by the "concentration speck" theory (Sheppard, Trivelli, and Loveland, *loc. cit.* p. 72) inasmuch as, in this theory, the process of growth of the nuclei is explicitly mentioned.

Two such modifications were considered and worked out in some detail; one, based upon the assumption that the rate of growth of the size (area) of the nuclei by accretion of silver atoms under the action of light is proportional to their instantaneous *perimeter*; and another in which this rate of growth was assumed to be proportional to their instantaneous *size* itself.

The former has led to a type of characteristic curves (k, E curves) clashing markedly with the experimental ones, and need not therefore be described here, and the latter, which thus far seems promising, is treated in the following part of the paper.

Rate of Growth of Nucleus Proportional to its Size.

Let s be the size, that is to say, the area * of a nucleus of silver before exposure, and σ' its size at any stage of its growth during the exposure by accretion of further silver atoms.

Without entering into the mechanism of this process, let us assume that, in the presence of light of sufficiently high frequency and intensity, each nucleus grows in size at a rate proportional to its instantaneous size and to the incident light-intensity I,

$$\frac{d\sigma'}{\sigma'} = cI dt = cdE, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where c is a coefficient which, for grains of a given size in a given emulsion, will be considered as a constant, but which may vary with the grain size and the kind of emulsion.

* If, indeed, it be the area of the nucleus which is relevant for its developability.

Notice that by the very assumption of proportionality of growth to I, the cases in which the reciprocity failure is pronounced are excluded. These may be taken into account by substituting for I itself some more complicated function of the intensity; also by requiring that if I falls below a certain value, there shall be no increase of the nuclei. For the present, however, we will assume that I lies within the limits of (approximate) validity of the reciprocity law. Since $\sigma' = s$ for $E = 0$, we have from (6)

$$\sigma' = se^{cE}.$$

In particular, let σ be the size of the nucleus at which it just becomes an "active" nucleus and thus makes the grain containing it developable *, and let E be the corresponding exposure. Then

$$se^{cE} = \sigma \; ; \; E = \frac{1}{c} \log \frac{\sigma}{s}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

a relation between the original size of a nucleus and the exposure required for maturing it.

The law (6), of course, is not supposed to hold indefinitely, but only up to a certain nucleus size exceeding σ, beyond which the growth must be imagined to be slowed down and eventually come to an end. A correspondingly modified differential equation, to replace (6), could easily be written down. Such a modification, however, which would introduce purely formal complications into our results, would be superfluous. For our only object is to find the number k of grains made developable by a given exposure E ; and since every grain whose nucleus has once attained the size σ becomes developable, the number k as a function of E will be entirely independent of the form of the law of growth beyond σ.

A grain of the emulsion will, in general, contain several nuclei of different sizes. Of these the largest, if all grow according to (6), will be the first to become an active nucleus and, therefore, to make the grain developable.

Now, let the number of grains whose *largest* nuclei are, before exposure, of size s to $s + ds$ be given by

$$Ae^{-h^2(s-s_0)^2} ds, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where A, h, and s_0 are constants. (Notice that this assumption differs essentially from that made in connexion with Toy's theory, where the "sensitivity" was taken to be normally distributed over *the nuclei*.) In the distribution

* The value of σ, which plays here the part of a constant, will, of course, vary with the development conditions.

law (8) the variable s will be expressed in terms of exposure according to (7), *i. e.*, by

$$s = \sigma e^{-cE}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In accordance with this let us still introduce a constant E_0 defined by

$$s_0 = \sigma^{-cE_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9_0)$$

The formula for the proportionate number of grains made developable by a given exposure can now be deduced without difficulty.

In fact, the number of grains with their largest nuclei ranging in original size from the limit value σ down to s, and therefore made developable by an exposure $E = \frac{1}{c} \log \frac{\sigma}{s}$, will be

$$k = A \int_s^\sigma e^{-h^2(s-s_0^2)} ds.$$

The upper limit of the integral corresponds to $E = \theta$ and the lower to the given exposure E. If Φ be again the error-function and C a constant proportional to A/h, the last formula can be written

$$k = C\{\Phi[h(\sigma - s_0)] - \Phi[h(s - s_0)]\}.$$

Let N be the total number of grains with nuclei ranging originally in size from $s = 0$ up to $s = \sigma$, that is to say, not counting the fog grains for which $s \geqslant \sigma$. Then we shall have $k = N$ for $s = 0$, and by the last equation,

$$N = C\{\Phi[h(\sigma - s_0)] + \Phi(hs_0)\}.$$

Thus, eliminating the constant C,

$$k = N \frac{\Phi[h(\sigma - s_0)] - \Phi[h(s - s_0)]}{\Phi[h(\sigma - s_0)] - \Phi(hs_0)}.$$

Ultimately, substituting s, s_0 from (9), (9$_0$), and putting for brevity

$$g = h\sigma, \quad \alpha = hs_0 = ge^{-cE_0}, \quad . \quad . \quad . \quad . \quad (10)$$

we have for the number k of grains made developable by an exposure E

$$\frac{k}{N} = \frac{\Phi(g - \alpha) - \Phi(ge^{-cE} - \alpha)}{\Phi(g - \alpha) + \Phi(\alpha)}. \quad . \quad . \quad . \quad . \quad (11)$$

This is the required formula. We may notice that if the law of growth (6) were retained, but the sizes s were assumed

to have a normal frequency distribution over the nuclei themselves (instead of the grains), as in the section on Toy's theory, then the same formula (11) would hold with k/N replaced by v/κ, where κ is the average number of nuclei per grain and $v = \log N/(N-k)$. But formula (11), as it stands, turned out to cover the observed facts much better. It has, moreover, the advantage of being free from the elusive factor κ or v_∞.

The original parameters h, σ, s_0 appear only through the two products g and α. These may be expected to retain the same values even for grains of different sizes within a given emulsion, while the coefficient c, appearing originally in the law of growth (6), is likely to vary with the size of the grain, and may even vary from grain to grain in the case of equal grains. For the growth of the relevant (*i. e.*, largest) nucleus will be influenced by the presence of other nuclei upon the same grain. Under these circumstances the constant coefficient c in (11) has to be considered as the result of averaging over a number of grains of equal size. In all, formula (11) contains three independent constants—g, α, and c. The parameter E_0 is defined by $cE_0 = \log \frac{\sigma}{s_0}$, and here s_0 is the mode of the frequency distribution (8).

The k, E curve (11) has, in general, an inflexion point, which makes it adaptable to the experimental characteristic curves. Its position, $x_i = cE_i$, is given by the vanishing of the second derivative of the variable part of k/N, say of

$$f(x) = \frac{\sqrt{\pi}}{2}\Phi[g(e^{-x} - e^{-x_0})], \text{ where } x = cE.$$

Write $u = g(e^{-x} - e^{-x_0})$. Then $f'(x) = -ge^{-u^2-x}$, and the equation $f''(x) = 0$ becomes

$$2u\frac{du}{dx} + 1 = 0$$

or

$$2g^2(e^{-x_i} - e^{-x_0}) = e^{x_i},$$

a quadratic for e^{x_i}, which gives

$$e^{x_i} = g^2 e^{-x_0}\left\{\sqrt{1 + \frac{2e^{2x_0}}{g^2}} - 1\right\} \quad . \quad . \quad . \quad . \quad (12)$$

Since x or cE is positive, an inflexion point will exist only

if the right-hand member of (12) is greater than 1, or

$$\sqrt{1+\frac{2e^{2x_0}}{g^2}} > 1+\frac{e^{x_0}}{g^2},$$

i. e.,

$$e^{x_0}\left(1+\frac{1}{2g^2}\right) > 1,$$

which can also be written

$$g\left(1-\frac{1}{2g^2}\right) > \alpha. \quad . \quad . \quad . \quad . \quad . \quad (12\,a)$$

In the numerical cases to be considered in the sequel, in which g amounts to some units while α does not much exceed unity, this inequality will be amply satisfied.

If, on the other hand, g is a small fraction (when there is no inflexion point), the functions Φ in (11) can all be identified with the first powers of their arguments, and formula (11) degenerates into

$$k/\mathrm{N} = 1-e^{-c\mathrm{E}},$$

which is of the same type as that following from the quantum theory of exposure. As has already been mentioned, the observed curves deviate considerably from this simple form, and call accordingly for large values of the coefficient g, amounting to some units.

One more theoretical point, relating to fog grains, may be mentioned here. Suppose that the assumed frequency distribution (8) of nuclear sizes holds also for $s > \sigma$, the largest nucleus size occurring at all. Then the number N_f of fog-grains will be given by

$$\mathrm{N}_f = \mathrm{A}\int_0^{\tau} e^{-h^2(s-s_0)^2}\,ds = \mathrm{C}\{\Phi[h(\tau-s_0)]-\Phi[h(\sigma-s_0)]\},$$

where C is the same constant as above, *i. e.*, given by

$$\mathrm{C}\{\Phi[h(\sigma-s_0)]+\Phi(hs_0)\} = \mathrm{N}.$$

Here $h(\tau-s_0)$, a pure number, can be assumed to be large enough (say of the order of two or three units) * to make $\Phi[h(\tau-s_0)] \doteq 1$. Thus

$$\frac{\mathrm{N}_f}{\mathrm{N}} = \frac{1-\Phi(g-\alpha)}{\Phi(\alpha)+\Phi(g-\alpha)}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Notice that N comprises the non-fogged grains only, so that the total number of grains is $\mathrm{N}+\mathrm{N}_f$. From (13) we see

* $\Phi(2) = 0{\cdot}995$, $\Phi(2{\cdot}5) = 0{\cdot}9996$, $\Phi(3) = 0{\cdot}99998$.

that if an emulsion contains but a small fraction of fog-grains, only large values of g, amounting to two or three units, will be admissible in representing the data obtained with such an emulsion ; the more so if α is not negligible.

Turning now to the experimental verification of the formula (11), let us first consider the complete set of data obtained in this laboratory on four size-classes of grains of the Slow Process emulsion, mentioned above.

In the following table (I.) the observed values of 100 k/N, the percentage of grains made developable, are those given in Sheppard, Trivelli, and Loveland's paper (*l. c.* p. 66), E being the "exposure" in arbitrary units, in this case proportional to the exposure time at constant light-intensity.

TABLE I.

Values of 100 k/N for Slow Process Emulsion.

E ...	4	$4\sqrt{2}$	8	$8\sqrt{2}$	16	$16\sqrt{2}$	32	$32\sqrt{2}$	64	$64\sqrt{2}$	128	a	c
Calc. ...	—	—	3·7	10·1	25·3	49·5	74·2	89·8	96·8	99·2	99·9	0·115	0·050
Obs. ...	—	—	2·6	10·5	30·4	52·0	72·4	82·8	89·3	93·0	96·1		
Calc. ...	5·4	14·7	33·7	59·5	81·4	93·3	98·1	99·6	100	100	100	0·3	0·115
Obs. ...	13·1	19·0	30·9	51·3	76·3	88·1	93·3	95·7	98·0	99·4	99·8		
Calc. ...	20·2	42·7	68·4	86·7	95·5	98·8	99·8	100	100	100	—	0·5	0·184
Obs. ..	25·3	45·9	69·1	85·1	93·4	96·7	98·9	99·5	99·9	100			
Calc. ...	49·6	74·3	89·9	96·8	99·2	99·9	100	—	—	—	—	0·7	0·285
Obs. ...	52·0	73·8	85·0	94·7	98·0	98·8	100	—	—	—	—		

The average grain sizes for the four classes were, in square microns,

$$a = 0{\cdot}115,\quad 0{\cdot}3,\quad 0{\cdot}5,\quad 0{\cdot}7,$$

with a common class breadth of 0·2. There was no perceptible fog. The theoretical values of k/N were calculated by means of formula (11) with constants determined after a good many trials. The values of the constants g and α finally chosen for the first class turned out to suit also the remaining three classes of grains, which called only for different values of the coefficient c or a contraction of the original curve along the exposure axis. Ultimately, the constants chosen for the whole set are

$$g = 3{\cdot}50,\quad \alpha = 1{\cdot}05,$$

so that, for all classes,

$$\frac{k}{N} = \frac{1}{1{\cdot}862}[1-\Phi(3{\cdot}50e^{-cE}-1{\cdot}05)] \quad . \quad . \quad (11\,a)$$

(where 1 has been written for $\Phi(2{\cdot}45)=0{\cdot}9995$), and

$$c=0{\cdot}050,\quad 0{\cdot}115,\quad 0{\cdot}184,\quad 0{\cdot}285$$

for the classes 1 to 4 respectively. The condition of absence of perceptible fog is amply satisfied by these values of g, α. In fact, substituting them into (13) one finds $100\,\frac{N_f}{N}=0{\cdot}016$.

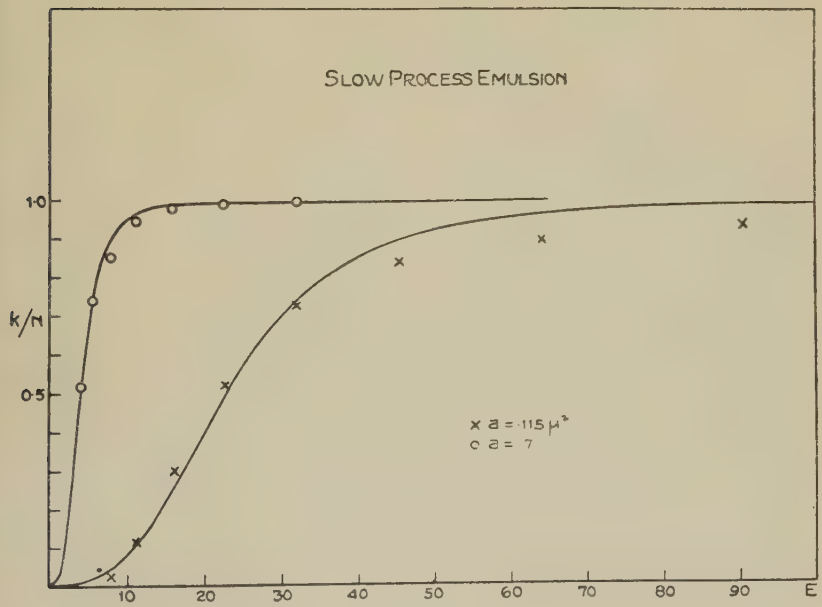


FIG. 1.

A graphic representation of these results is given in fig. 1 for the first and the fourth, and in fig. 2 for the second and the third classes of grains. The theoretical curves, especially those for class 3 and class 4, seem to follow the observed points closely enough, the deviations being on the whole irregular and scarcely exceeding the limits of the experimental error in determining the numbers k. Only the upper part of the first and, to a lesser extent, that of the second-class curve are systematically a few per cent. above

the points representing the observations. This, however, does not much disturb the characteristic similarity of the theoretical and the experimental curves.

The following is an interesting property of this set. The ratios of the values of the coefficient c for the four classes are

$$c_1 : c_2 : c_3 : c_4 = 10 : 23 : 37 : 57,$$

while

$$a_1 : a_2 : a_3 : a_4 = 10 : 26 : 43 : 61.$$

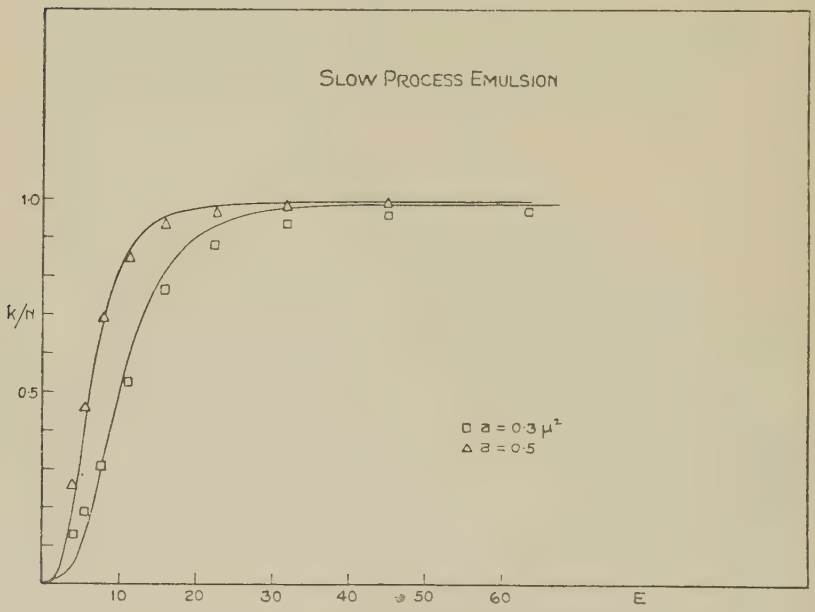


FIG. 2.

Thus the coefficient c increases but a little more slowly than the size (area) of the grains. In fact, the four values of c/a being

$$0{\cdot}43, \quad 0{\cdot}38, \quad 0{\cdot}37, \quad 0{\cdot}41,$$

c may, within the limits of experimental error, be taken to be proportional to the size a. If the mean of these four values is adopted, $c = 0{\cdot}40\,a$. Approximately, therefore, k depends in this case on the product Ea only (incident light flux per grain), the data for all four classes being represented by the single formula (11 a) with the exponent $c\mathrm{E}$ replaced by $0{\cdot}40\,Ea$. The dependence of the photographic effect upon Ea alone, which on the quantum theory appeared as an essential property, may of course be only a peculiarity of this

emulsion without, for the present, deserving to be considered as a general rule.

At any rate the totality of the data is fairly well represented by the formula (11 *a*). The corresponding curve is redrawn in fig. 3 with $x=cE$ as abscissa, the observed values of k/N for all four classes of grains being now plotted against x, with the original c-values. (The observed "points" are marked by crosses, squares, triangles, and circlets for the 1st to 4th classes respectively.)

Thus far the Slow Process emulsion.

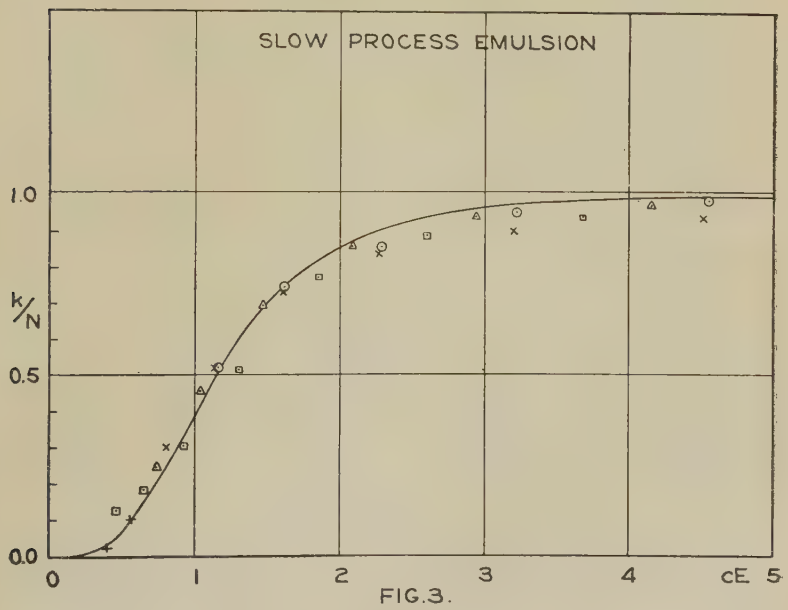


FIG. 3.

In the next place we will consider the experimental results obtained by Toy with the Ilford Process emulsion. Dr. Toy * gives two sets of his "smooth-curve" values of the percentage of grains (100 k/N) made developable by light of different intensities at constant exposure time, one set for grains of diameter 0·75 μ and another for grains of diameter 0·60 μ. The former, a rather short set (starting from the high percentage 35·5), cannot be adequately represented by our formula (11), but the latter set agrees with this formula well enough. This set of observed values is arrayed in the third row of Table II. The numbers of the second row are

* Phil. Mag. vol. xlv. p. 720 (1923).

calculated according to formula (11), with the constants

$$g=2\cdot50, \quad \alpha=0\cdot25, \quad \text{and} \quad c=7\cdot37.$$

The relative exposures E are identified with Toy's relative intensities (at constant exposure time).

Table II.

E ...	0·050	·075	·100	·150	·200	·250	·300	·350	·400	·450	·500
100 k/N calc. ...	2·8	7·2	14·1	32·4	50·8	65·5	76·3	83·7	88·8	92·3	94·6
obs. ...	2·0	7·0	16·0	35·5	52·0	63·5	73·0	79·0	84·5	89·8	93·5

A graphic representation of these results is given in fig. 4.

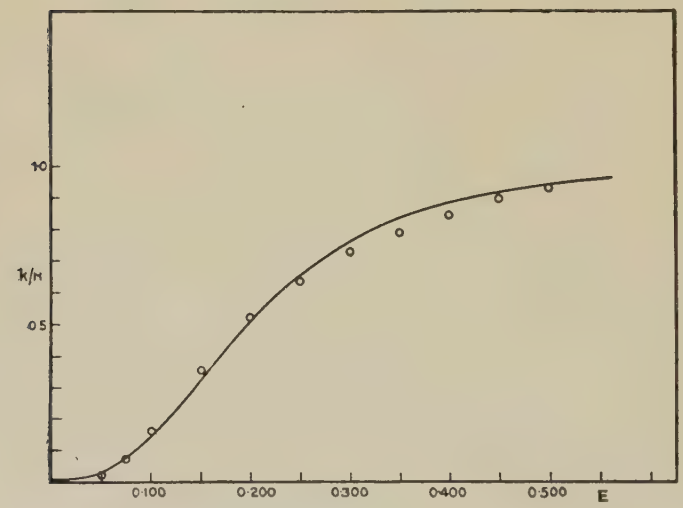


FIG. 4.

The agreement between the calculated and the observed values is fairly close, the largest difference being 4·7. The small residues could still be reduced somewhat by slightly modifying the constants, but this is hardly worth the trouble, especially as, the original observations not being quoted, the amounts carried away by Toy's smoothing process are unknown. The percentage of fog-grains corresponding to the adopted values of g, α would, by (13), be as low as 0·12 per cent., and thus again imperceptible. As Toy's computation method is independent of the number of fogged grains present, no such number is quoted in his paper, so

that in this respect no definite objection can be raised against these values of the constants.

Further, we may apply the formula (11) to some unpublished experimental results obtained in this laboratory by Trivelli and Loveland (July 1926) on the Eastman 40 emulsion. These data consist of three sets, relating to grains of size 0·4, 0·8, 1·2 μ^2. The first class of grains, for which the results are

E	1	$\sqrt{2}$	2	$2\sqrt{2}$	4	$4\sqrt{2}$	8	$8\sqrt{2}$	16	$16\sqrt{2}$	32	$32\sqrt{2}$
100 k/N ...	1·1	3·2	7·4	10·6	15·5	22·2	27·6	38·9	46·3	54·6	58·2	62·3,

shows the peculiar behaviour that its k/N-values tend with increasing exposure * apparently to 0·62 or 0·65 instead of unity, as if about 35 per cent. of these, the smallest grains, were completely insensitive to the applied intensity of light (i. e., $s \leqslant \sigma$, and not growing at that light-intensity). This state of things cannot be represented by the theory under discussion without modifying essentially our assumption about the law of growth or the size-distribution law of the nuclei, unless one decided to consider as N only the fraction 0·65 of all grains originally present. The data for the second-, and especially the third-size class of grains ($a=1·2$), do not show this peculiar tendency, and can be covered by our formula (11) rather closely, as will be seen from Table III. and the corresponding graph (fig. 5). As a number of trials have shown, about the best agreement is obtained when the constants in formula (11) are given the values

$$g=1·00, \quad \alpha=0·50, \quad c=0·311\,;$$

with these the numbers of the second row of the tables were calculated.

Table III.

E	1	$\sqrt{2}$	2	$2\sqrt{2}$	4	$4\sqrt{2}$	8	$8\sqrt{2}$	16	$16\sqrt{2}$	32	$32\sqrt{2}$
100 k/N calc. ...	25·2	34·6	46·0	62·4	73·0	84·2	92·7	97·4	99·3	99·9	100	100
obs.	21·5	35·2	43·0	62·7	72·7	85·8	93·5	95·3	(95·3)	99·4	99·4	99·4

The values of g, α, however, would imply, by (13), the presence of a very high percentage of fog-grains, namely little less than 32 per cent., which of course is out of the question. (The constants $g=1·40$, $\alpha=0·25$, and $c=0·43$, giving a somewhat less close but still tolerable agreement

* Increasing exposure time, that is, at constant intensity.

with the observed k/N, would reduce the theoretical fog to 8 per cent., but even this may be too high ; the actual fog, if any, scarcely exceeded 2 or 3 per cent.) Thus, if, in view of the close agreement exhibited by the last table, we wished to retain these values of g, α, we would have to assume that, in this emulsion at least, pre-exposure nuclei larger than σ are comparatively rare ; *i. e.*, that for $s > \sigma$ the number of grains having such nuclei diminishes more rapidly than would correspond to the normal frequency distribution (8). This would evidently make the number of

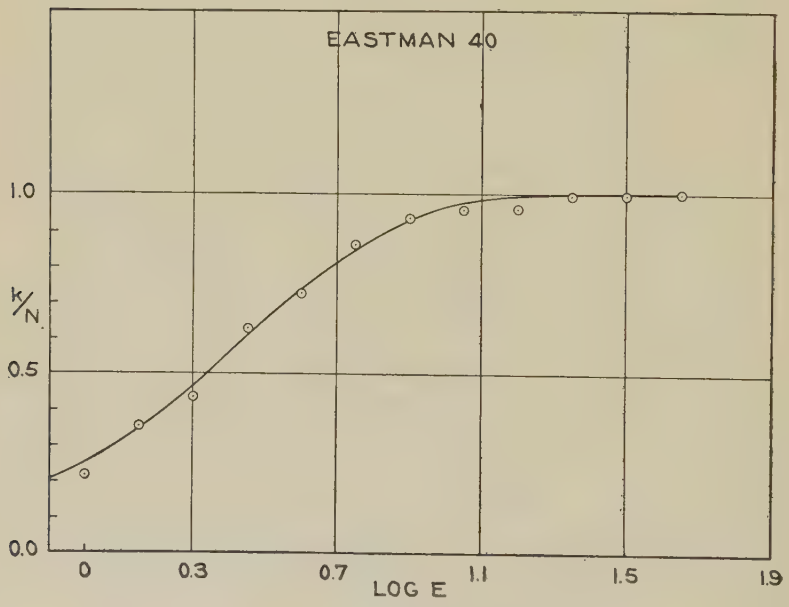


FIG. 5.

fog-grains smaller than that required by (13). Yet it must be admitted that, although not unlikely, such a hypothesis, introduced *ad hoc*, is not very satisfactory.

For the present but one more set of experimental data is available, and will be considered here. These, not yet published, were recently obtained in this laboratory by Trivelli and Loveland with a pure bromide emulsion. The grains were divided into four size-classes, ranging from 0·02 to 1·5, 1·5 to 3·0, etc., up to $6\mu^2$, and a "remainder" extending from $6\mu^2$ upwards. The results, k/N as function of exposure time at constant intensity, were for the first

four classes utterly irregular, and only the last class could at all be utilized for the purpose in hand. The observed (not smoothed) values of 100 k/N are given in the last row of Table IV., the numbers of the second row being calculated by formula (11), with the constants

$$g=1{\cdot}25, \quad \alpha=0{\cdot}40, \quad \text{and} \quad c=0{\cdot}133.$$

TABLE IV.

E	1	$\sqrt{2}$	2	$2\sqrt{2}$	4	$4\sqrt{2}$	8	$8\sqrt{2}$	16	$16\sqrt{2}$
100 k/N										
calc.	8·1	11·6	16·8	24·0	34·0	46·7	61·4	75·8	87·4	95·0
obs.	7·6	—	20·5	(32·2)	33·3	45·6	57·9	74·6	88·6	98·3

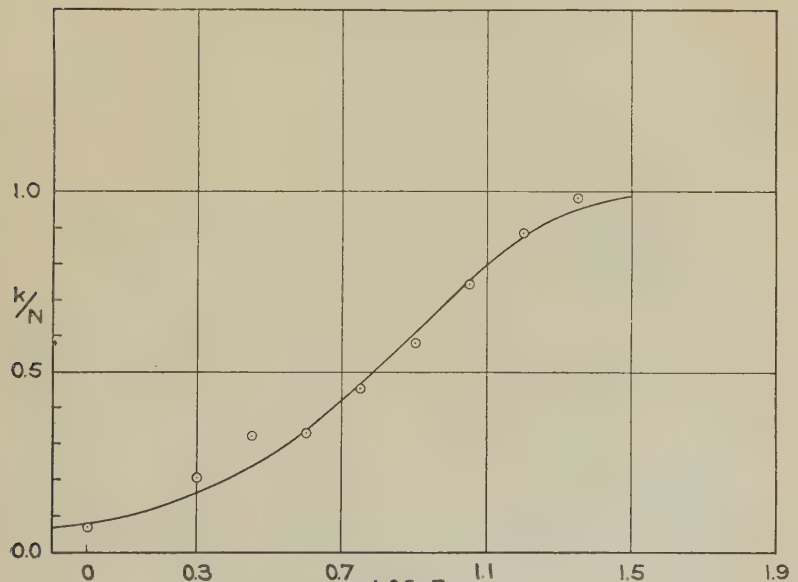


FIG. 6.

The agreement, as shown also in fig. 6, seems in itself quite satisfactory. But these values of g, α would again imply through (13) the presence of too many fog-grains, though not so many as in the preceding case, viz., 16 per cent. The above-said limitation of the distribution law (8) would then again have to be applied.

To sum up, the formula (11) for the number of grains made developable by a given exposure, based upon the size-frequency distribution (8) and the law of growth (6) of the nuclei, can be said to represent the greater part of the

available experimental data with fair accuracy, the deviations being mostly within the limits of experimental error. The number of fog-grains ($s>\sigma$), however, implied by the best values of g, α is, according to the subsidiary formula (13), in two cases much too large ; and since the latter formula is a direct consequence of the distribution law (8), this would have to be replaced by a frequency which beyond σ falls off more rapidly. Whenever $g-\alpha$ is large enough (say only 1·5), as in most cases considered above, this difficulty does not arise, and it remains to be seen whether such will not be also the case of the majority of future experimental findings.

A Refinement of the Main Formula. Effect of Finite Size of and Competition between the Nuclei.

Formula (11) for the number of grains affected by a given exposure is capable of a certain refinement which, though verifiable only on much more accurate data than those hitherto available, has even at this stage seemed to offer some interest.

In deriving that formula, account was taken only of a single nucleus for each grain, namely the largest of those present upon the grain ; and its logarithmic rate of growth was assumed to be proportional to the incident light-intensity, the coefficient c being supposed constant. This assumption, expressed by (6), gave the simple relation $s/\sigma=e^{-cE}$.

Now, since the nuclei grow, simultaneously, by accretion of silver atoms derived more or less directly from the whole grain, it is reasonable to assume that the (logarithmic) rate of growth of each nucleus is, *ceteris paribus*, some function of that part of the area of the grain which is not occupied by nuclei formed up to the given instant. The nuclei being very small compared with the grain, such a modification of our original assumption will affect the final result only to a small degree. Yet the effect may turn out to be perceptible, and it has therefore seemed worth while to derive the consequence of the proposed modification.

Let us then consider a grain having $\kappa+1$ nuclei of initial sizes $s, s_1, s_2, \ldots s_\kappa$, of which s is the largest. Let $\sigma', \sigma_1', \sigma_2', \ldots \sigma_\kappa'$ be their sizes at any stage t of growth, and a the size of the grain. Then the modified assumption may be written

$$\left.\begin{aligned} \frac{d\sigma'}{\sigma'} &= f(a-\sigma'-\sigma_1'-\sigma_2'-\ldots-\sigma_\kappa')\mathrm{I}\,dt, \\ \frac{d\sigma_1'}{\sigma_1'} &= f(a-\sigma'-\sigma_1'-\sigma_2'-\ldots-\sigma_\kappa')\mathrm{I}\,dt, \text{ etc.,} \end{aligned}\right\} \quad (14)$$

where the form of the function f, which will be left unspecified, may vary from emulsion to emulsion. Thus, for instance, in the case of the four classes of the Slow Process emulsion f would be nearly proportional to its argument. $\Sigma\sigma''$ being small compared with a, and also (as we will assume) compared with $f(a)/f'(a)$, we can write

$$f(a-\sigma'-\sigma_1'-\ldots-\sigma_\kappa')=c\,[1-\beta(\sigma'+\sigma_1'+\ldots+\sigma_\kappa']\,,$$

where $$c=f(a),\quad \beta=f'(a)/f(a).$$

The right-hand members of the $\kappa+1$ equations (14) being all equal, we have, for $i=1, 2, \ldots \kappa$,

$$\frac{d\sigma_i'}{\sigma_i'}=\frac{d\sigma'}{\sigma'},$$

whence $\log\frac{\sigma_i'}{\sigma'}=$ const., $\sigma_i'/\sigma'=$ const., *i. e.*,

$$\sigma_i'/\sigma'=s_i/s. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

In fine, all the nuclei upon the same grain grow proportionally to each other. It is thus enough to consider only one of the equations (14). We will take that for the largest nucleus, since this decides the final developability of the grain. Thus, introducing (15) into the first of (14), and writing $\mathrm{I}dt=d\mathrm{E}$,

$$\frac{d\sigma'}{\sigma'}=c\left[1-\beta\sigma'\left(1+\frac{s_1}{s}+\frac{s_2}{s}+\ldots+\frac{s_\kappa}{s}\right)\right]d\mathrm{E},$$

or, putting

$$\zeta=1+\frac{s_1}{s}+\frac{s_2}{s}+\ldots+\frac{s_\kappa}{s},$$

which for a given strain is a constant,

$$\frac{d\sigma'}{\sigma'(1-\beta\zeta\sigma')}=\left[\frac{1}{\sigma'}-\frac{1}{\sigma'-\frac{1}{\beta\zeta}}\right]d\sigma'=cd\mathrm{E}.$$

Thus $$\sigma'\Big/\left(\sigma'-\frac{1}{\beta\zeta}\right)=\mathrm{A}e^{c\mathrm{E}},\quad \mathrm{A}=\text{const.},$$

and since $\sigma'=s$ for $\mathrm{E}=0$,

$$\frac{\sigma'(1-\beta\zeta s)}{s(1-\beta\zeta\sigma')}=e^{c\mathrm{E}}.$$

In particular, if $\sigma'=\sigma$ be the size at which the nucleus

becomes developable, and E the exposure which makes it grow from s to σ,

$$\frac{\sigma}{1-\beta\zeta\sigma} = \frac{s}{1-\beta\zeta s} e^{c\mathrm{E}}.$$

Since $\beta\sigma$, and even $\zeta\beta\sigma$, will be a small fraction of unity, and the more so $\zeta\beta s$, we have, up to second-order terms,

$$\frac{\sigma}{s}[1+\beta\zeta(\sigma-s)] = e^{c\mathrm{E}},$$

and here we may put, in the small correction term, $s=\sigma e^{-c\mathrm{E}}$.

Thus, ultimately,

$$\left.\begin{aligned} s/\sigma &= e^{-c\mathrm{E}}[1+\beta\zeta\sigma(1-e^{-c\mathrm{E}})], \\ \zeta &= 1+\frac{1}{s}(s_1+s_2+\ \ldots\ +s_\kappa), \end{aligned}\right\} \quad . \quad . \quad (16)$$

c being some function of a, and $\beta = c'(a)/c(a)$. This value of s/σ, replacing the original expression $e^{-c\mathrm{E}}$, is now to be substituted into the previous equation :

$$\frac{k}{\mathrm{N}} = \frac{\Phi(g-\alpha)-\Phi\left(g\frac{s}{\sigma}-\alpha\right)}{\Phi(g-\alpha)+\Phi(\alpha)}, \quad . \quad . \quad . \quad (17)$$

giving the number of grains k made developable by an exposure E. The departure from the original formula (11) will depend on $\beta\zeta\sigma$. (Notice that β is a reciprocal area. If c is proportional to a, then $\beta = 1/a$.)

The value of the coefficient ζ of the correction term may vary from grain to grain, the number of nuclei $(\kappa+1)$ as well as their relative sizes, $\frac{s_1}{s}$, $\frac{s_2}{s}$, etc., being different for different grains, even if the latter be all of the same size a. But in applying formula (16), we may as well take for ζ a unique number, to be considered as an average value of this grain-coefficient. Thus $\kappa+1$ can be replaced by the average number of nuclei per grain, and for every ratio s_i/s the mean of these ratios can be taken, for which some reasonable value, such as $\frac{1}{2}$, may be provisionally adopted. This would give

$$\zeta = 1+\kappa\left(\frac{\bar{s}_i}{s}\right) = 1+\tfrac{1}{2}\kappa,$$

where, of course, $\kappa+1$, the average number of all nuclei per grain, would still remain unknown and to be determined

experimentally. Thus far, data of this kind, apart from a few probably incomplete results (disclosing perhaps only some of the nuclei), due to Svedberg and Toy, do not seem to be available. Still less known is σ, the minimum size of an "active" or developable nucleus. This, moreover, will depend on the development. Under such circumstances the whole coefficient $\beta\zeta\sigma$ of the correction term in formula (16) would have, for the present, to be considered as one more empirical parameter, in addition to the main parameters g, α, c, to be adapted to the observed k, E curves.

Rochester, N.Y.
October 3, 1927.

L. *On the Coefficient of Sound-absorption Measured by the Reverberation Method.* *By* E. T. Paris, *D.Sc.**

THERE are several methods of measuring the coefficients of sound-absorption for different materials †. In the reverberation method of W. C. Sabine a specimen of the material to be tested is mounted inside a reverberation-chamber, and the coefficient of absorption (defined as the ratio of the difference between the incident and reflected energy-fluxes to the incident energy-flux) is deduced from the observed effect of the presence of the specimen on the rate of decay of sound in the chamber. According to the theory of reverberation, the specimen receives sound at all angles of incidence from 0° to 90°.

There are, however, other methods of measuring sound-absorption in which plane-waves of sound are made to impinge on a specimen at some definite angle of incidence. For example, in Watson's experiments a beam of sound (produced by means of a source at the focus of a paraboloidal reflector) was directed on to the specimen to be tested. In this method the angle of incidence is determined at will by snitably arranging the relative positions of the specimen and the reflector. Again, in the stationary-wave method sound-waves fall normally on the specimen, the coefficient of absorption being deduced from observations on the interference pattern in front of the specimen.

In general the coefficient of absorption of a given substance is a function of the wave-length of the sound and of

* Communicated by the Author.

† A description of the methods at present in use is given by Davis and Kaye, 'Acoustics of Buildings,' chap. v. (Bell, 1927).

the angle of incidence, so that the value of the coefficient obtained by the reverberation method cannot be expected to agree with that obtained by one of the other methods mentioned above.

In the present paper an attempt is made to correlate the coefficient of absorption of a substance, measured at some particular wave-length and expressed as a function of the angle of incidence, with the coefficient of absorption determined by Sabine's reverberation method for the same wave-length.

The coefficient measured by Sabine's method will be called the "reverberation coefficient of absorption" and denoted by α_r. The coefficient of absorption for waves incident at an angle θ will be denoted by $\alpha(\theta)$.

The theory of reverberation as developed by Sabine, Jäger, and others is a departure from classical methods in theoretical acoustics, and involves certain assumptions regarding the distribution and behaviour of sound-energy in an enclosed space in which reverberation is occurring. Accounts of the theory and of the assumptions made have been given in recent years by E. A. Eckhardt * and E. Buckingham †. The question of the validity of the assumptions involved will not be discussed here, but attention will be confined to examining the result of introducing the coefficient $\alpha(\theta)$ into the theory of reverberation with the object of finding a relation between $\alpha(\theta)$ and α_r.

The rate at which sound-energy strikes the walls of a room in which reverberation is occurring is found as follows ‡. Let $d\mathrm{S}$ be an element of area of the wall of a room in which the acoustical energy-density ρ is uniform, and let $d\mathrm{V}$ be an element of volume at a distance r from $d\mathrm{S}$ in a direction making an angle θ with the normal n to $d\mathrm{S}$ (fig. 1). Of the energy $\rho\, d\mathrm{V}$ contained within $d\mathrm{V}$ at any instant, that portion will ultimately strike $d\mathrm{S}$ which is moving within directions included within the solid angle

$$d\omega = d\mathrm{S} \cos\theta / r^2$$

subtended by $d\mathrm{S}$ at $d\mathrm{V}$. This fraction is $d\omega/4\pi$, so that the amount of energy inside $d\mathrm{V}$ which will ultimately strike $d\mathrm{S}$ is

$$(\rho\, d\mathrm{V}\, d\mathrm{S} \cos\theta) \,/\, (4\pi r^2).$$

The total amount of sound-energy that falls on $d\mathrm{S}$ in one

* Journ. Franklin Inst. cixv. p. 799 (1923).
† Sci. Paper of the Bureau of Standards, No. 506 (1925).
‡ *Cf.* Buckingham, *loc. cit.* p. 201.

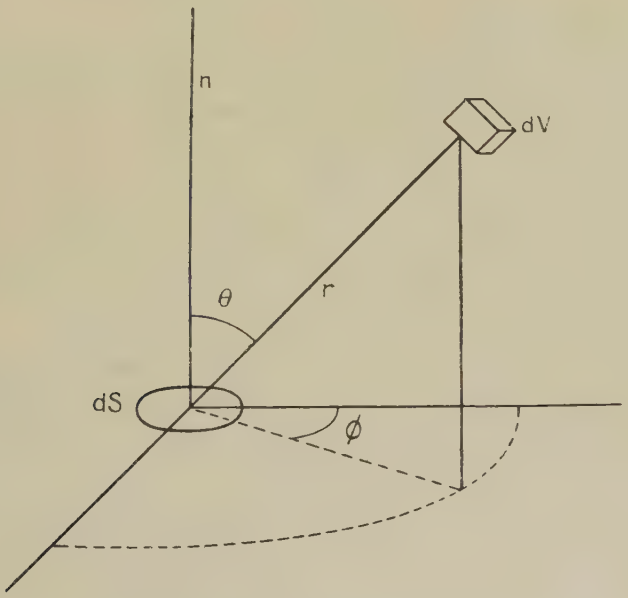
second is obtained by integrating this expression throughout a hemisphere of radius a described about $d\mathrm{S}$ as centre, a being the distance traversed by sound in one second. Thus, using polar coordinates r, θ, ϕ (fig. 1) so that

$$d\mathrm{V} = r^2 \sin\theta \, dr \, d\theta \, d\phi,$$

we have for the rate at which sound-energy falls on $d\mathrm{S}$:

$$\frac{\rho \, d\mathrm{S}}{4\pi} \int_0^a dr \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta \, d\theta = \frac{\rho a \, d\mathrm{S}}{4} \quad . \quad . \quad (1)$$

Fig. 1.



The rate at which sound is absorbed at $d\mathrm{S}$ is

$$\alpha_r \left(\frac{\rho a \, d\mathrm{S}}{4} \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α_r is the reverberation absorption-coefficient appropriate to the surface of which $d\mathrm{S}$ forms a part.

Another expression for the rate at which sound is absorbed at $d\mathrm{S}$ can be formed by making use of the coefficient $\alpha(\theta)$. Thus the rate at which energy coming from $d\mathrm{V}$ is absorbed at $d\mathrm{S}$ is

$$\alpha(\theta) \, . \, (\rho \, d\mathrm{V} \, d\mathrm{S} \cos\theta) / (4\pi r^2),$$

and hence the total rate of sound-absorption at $d\mathrm{S}$ is

$$\frac{\rho\, d\mathrm{S}}{4\pi}\int_0^a dr\int_0^{2\pi} d\phi\int_0^{\pi/2}\alpha(\theta)\sin\theta\cos\theta\, d\theta$$

$$=\frac{\rho a\, d\mathrm{S}}{2}\int_0^{\pi/2}\alpha(\theta)\sin\theta\cos\theta\, d\theta. \quad . \quad (3)$$

By equating the expressions (2) and (3) for the rate at which sound is absorbed at $d\mathrm{S}$, we find

$$\alpha_r = 2\int_0^{\pi/2}\alpha(\theta)\sin\theta\cos\theta\, d\theta. \quad . \quad . \quad . \quad (4)$$

This equation provides a means for finding α_r when $\alpha(\theta)$ is known. It is clear, however, that in general the determination of α_r in this way would be very laborious, for it would be necessary to find $\alpha(\theta)$ for all values of θ between 0 and $\pi/2$ (probably with apparatus of the type used by Watson) before the integration in (4) could be effected. Incidentally, equation (4) shows that a simple determination of the coefficient of absorption at normal incidence, that is $\alpha(0)$, by stationary-wave or other small-scale testing apparatus, supplies insufficient data for calculating the reverberation coefficient α_r.

There is, however, a class of substances for which the difficulty of finding $\alpha(\theta)$, and thence α_r by means of equation (4), is not great. The substances referred to are the porous acoustic tiles and plasters used in architectural acoustics. For such materials it is possible to determine a quantity called the "acoustical admittance per unit area of reflecting surface" from which the coefficient of absorption at any angle of incidence, $\alpha(\theta)$, can readily be calculated *.

Substances of this type absorb sound by virtue of the fact that during reflexion there is a movement of air into and out of the pores of the material. If the pores are small this in-and-out movement of air is accompanied (owing to viscosity) by the degradation of sound-energy into heat. If Φ is the velocity-potential due to incident and reflected sound-waves at the surface of a porous medium of the kind indicated, and q is the volume of air per unit area of surface moving periodically in and out of the pores, then $q=\Omega\Phi$, where Ω is the "acoustical admittance per unit area of reflecting surface."

An ideal substance of the type contemplated would consist of a flat solid wall perforated by a great number of pores,

* Proc. Roy. Soc. A, cxv. p. 407 (1927).

bounded by surfaces everywhere perpendicular to the flat face of the wall. The characteristic feature of such a reflecting surface is that sound-waves are produced only in the pores and not in the solid material itself. Also the wave-motion in the pores is not transmitted internally from one part of the reflecting surface to another, so that Ω is independent of the angle of incidence. Acoustic tiles and plasters, while not conforming precisely to this specification, appear to do so to an extent which justifies the employment of an "acoustical admittance" (assumed independent of the angle of incidence) in connexion with the investigation of their acoustical properties.

It can be shown * that the coefficient of absorption of a porous substance of the kind under consideration can be expressed in terms of acoustical admittance per unit area as follows :—

$$\alpha(\theta) = 1 - \left| \frac{\cos\theta - a\Omega}{\cos\theta + a\Omega} \right|^2, \quad . \quad . \quad . \quad . \quad (5)$$

where a is the velocity of sound, and θ, as before, is the angle of incidence. If Ω is separated into its real and imaginary parts, say $\Omega = \Omega_1 + i\Omega_2$, then

$$\alpha(\theta) = \frac{4a\Omega_1 \cos\theta}{\cos^2\theta + 2a\Omega_1 \cos\theta + a^2(\Omega_1^2 + \Omega_2^2)}. \quad . \quad (6)$$

By substituting this value for $\alpha(\theta)$ in (4), we obtain

$$\alpha_r = 8a\Omega_1 \int_0^{\pi/2} \frac{\cos^2\theta \sin\theta \, d\theta}{\cos^2\theta + 2a\Omega_1 \cos\theta + a^2(\Omega_1^2 + \Omega_2^2)}. \quad (7)$$

Let

$$x = \cos\theta, \quad A = a^2(\Omega_1^2 + \Omega_2^2), \quad \text{and} \quad B = 2a\Omega_1.$$

Then, since $4A - B^2 > 0$,

$$\alpha_r = 4B \int_0^1 \frac{x^2 \, dx}{x^2 + Bx + A}$$

$$= 4B \left[x - \tfrac{1}{2}B \log_e (x^2 + Bx + A) + \frac{B^2 - 2A}{\sqrt{(4A - B^2)}} \tan^{-1}\left(\frac{2x + B}{\sqrt{(4A - B^2)}} \right) \right]_0^1. \quad (8) \dagger$$

* Proc. Roy. Soc. A, cxv. p. 418 (1927).

† Peirce, 'Short Table of Integrals,' p. 9 (Ginn & Co.).

Or, putting in the values of A and B,

$$\alpha_r = 8a\Omega_1\left[1-a\Omega_1\log_e\frac{(1+a\Omega_1)^2+(a\Omega_2)^2}{a^2(\Omega_1^2+\Omega_2^2)} + \frac{a^2(\Omega_1^2-\Omega_2^2)}{a\Omega_2}\left\{\tan^{-1}\left(\frac{1+a\Omega_1}{a\Omega_2}\right) - \tan^{-1}\left(\frac{a\Omega_1}{a\Omega_2}\right)\right\}\right]. \quad (9)$$

By means of (2) the reverberation coefficient can be calculated for any porous reflecting surface for which the acoustical admittance per unit area is known.

For example, a determination was made, by means of stationary-wave apparatus, of the acoustical admittance of "Akoustolith" tile (supplied through the Building Research Board of the Department of Scientific and Industrial Research) at 512 vibrations per second. Details of the apparatus employed and the method of finding "acoustical admittance" have been given elsewhere *. The value obtained for Ω was $0{\cdot}0641-\iota\times 0{\cdot}0643$, and inserting this value in (5) and (9), we find that $\alpha(0)=0{\cdot}23$ and $\alpha_r=0{\cdot}35$. Thus, according to this calculation, the reverberation coefficient is considerably greater than the coefficient at normal incidence †.

The calculated value of α_r agrees well with that quoted by Watson ‡ for Akoustolith tile at 512 vibrations per second, viz. 0·36. Davis and Kaye §, however, quoting results obtained at the Building Research Station of the Department of Scientific and Industrial Research by a reverberation method, give the surprisingly low value of 0·19 for the coefficient at the same frequency, this being less than the coefficient at normal incidence. There appears, therefore, to be some uncertainty as to the true value of the reverberation absorption-coefficient of this substance, and no conclusion can safely be drawn as to whether the calculated value of α_r is or is not confirmed by experiment.

The absorption of sound by an ideal porous substance,

* The apparatus is described in Proc. Phys. Soc. xxxix. p. 274 (1927); the method of finding Ω is given in Proc. Roy. Soc. A, cxv. p. 413 (1927).

† The value of 0·23 for $\alpha(0)$ is less than that given in an earlier paper, viz. 0·26 (Proc. Phys. Soc. xxxix. p. 281, 1927); this may be due to the fact that the specimen used in the present test was an old one and had suffered some damage which had been repaired with plaster of Paris.

‡ 'Acoustics of Buildings,' p. 25.

§ 'Acoustics of Buildings,' p. 116.

presenting a flat surface to the incident sound, and perforated by a large number of similar channels bounded by surfaces perpendicular to the face, was the subject of a theoretical investigation by Rayleigh *. It has been pointed out in a previous paper † that, in the special case when the pores are so long that the vibrations within them are sensibly extinguished before the stopped ends are reached, the acoustical admittance per unit area (derived from equations given by Rayleigh) has a specially simple form, being proportional to the fraction of the area of the reflecting face which is occupied by the pore-openings. If σ is the perforated and σ' the corresponding unperforated area,

$$a\Omega = \sigma/(\sigma+\sigma'). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The coefficient of absorption at an angle θ is, by (5),

$$\alpha(\theta) = \frac{4a\Omega\cos\theta}{(a\Omega+\cos\theta)^2}, \quad . \quad . \quad . \quad . \quad (11)$$

which becomes unity when $\cos\theta = a\Omega$, so that there is always some angle of incidence, given by $\cos\theta = \sigma/(\sigma+\sigma')$, at which total absorption occurs. With $B = 2a\Omega$ we have, instead of (8),

$$\alpha_r = 4B\int_0^1 \frac{x^2\,dx}{(x+\frac{1}{2}B)^2}$$

$$= 8a\Omega\left\{\frac{1+2a\Omega}{1+a\Omega} - 2a\Omega\log_e\frac{1+a\Omega}{a\Omega}\right\}. \quad (12)\ ‡$$

Some numerial results obtained by means of (11) and (12) are given in the following table and serve (in the absence of

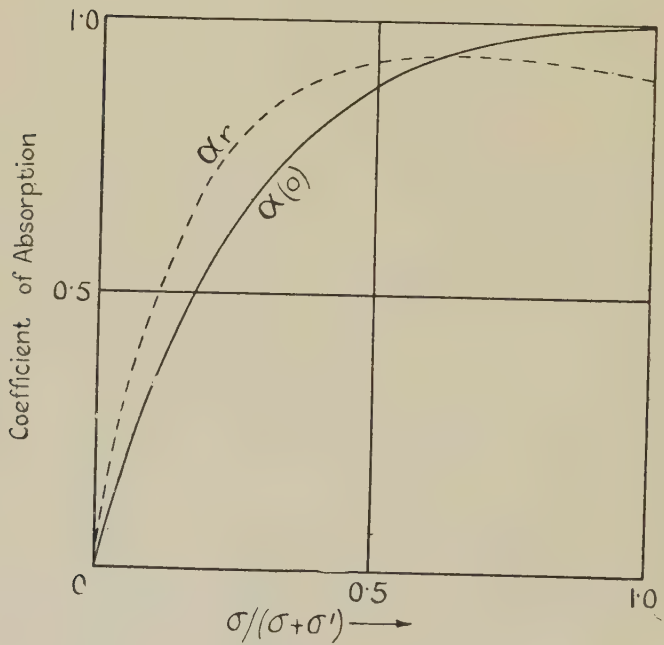
$\sigma/(\sigma+\sigma')$.	θ_m.	$\alpha(0)$.	α_r.
	° ′		
0·05	87 08	0·18	0·30
·1	84 15	·33	·49
·2	78 28	·56	·72
·3	72 32	·71	·84
·5	60 00	·89	·94
·7	45 34	·97	·95
·9	25 50	·997	·93
1·0	00 00	1·000	·91

* Phil. Mag. xxxix. p. 225 (1920); Sci. Papers, vi. p. 662.
† Proc. Roy. Soc. A, cxv. p. 413 (1927).
‡ Peirce, 'Short Table of Integrals,' p. 6 (Ginn & Co.).

data concerning substances actually employed for absorbing sound) to indicate how a reverberation coefficient may differ from the coefficient at normal incidence. The first column gives the value of $a\Omega$, or $\sigma/(\sigma+\sigma')$; the second column gives the value (θ_m) of the angle of incidence at which total absorption occurs ; the third and fourth columns give the values of $\alpha(0)$ and α_r calculated from (11) and (12) respectively.

If the figures in the last two columns are plotted against

Fig. 2.



$\sigma/(\sigma+\sigma')$ as in fig. 2, it is seen that $\alpha_r=\alpha(0)$ when $\sigma/(\sigma+\sigma')=0{\cdot}65$ approximately, α_r being greater than $\alpha(0)$ when $\sigma/(\sigma+\sigma')$ is smaller than this value and less than $\alpha(0)$ when it is greater. The rise in α_r as $\sigma/(\sigma+\sigma')$ is increased from 0 to 0·3 is very rapid, but little can be gained by making the proportion of perforated area greater than 0·3.

The reverberation coefficient passes through a maximum value of about 0·95 when $\sigma/(\sigma+\sigma')$ is between 0·6 and 0·7,

that is when θ_m is between 45°·5 and 53°·1. This result is in accordance with the fact that the amount of energy incident at an angle θ on an element of surface is proportional to $\sin 2\theta$, and is a maximum when $\theta = 45°$. It is therefore reasonable that α_r should be a maximum when θ_m, the angle at which total absorption occurs, is in the neighbourhood of 45°.

In conclusion, it should perhaps be emphasized that the results obtained in this paper are dependent on the assumption made in the theory of reverberation as to the behaviour of acoustical energy in an enclosed space. Interference is entirely ignored. The justification for this assumption is that it provides a theoretical basis for the reverberation formulæ which have been used with such striking success in auditorium acoustics. It remains to be seen whether its employment for establishing a relation between reverberation coefficients of absorption and those obtained by other methods will be justified by experimental results.

The investigation described in this paper was undertaken in connexion with experiments on sound-absorption carried out in the Acoustical Section of the Air Defence Experimental Establishment with the aid of funds provided by the Department of Scientific and Industrial Research on the recommendation of their Physics Research Board.

Summary.

A formula is deduced from reverberation theory by means of which the reverberation coefficient of absorption of a material can be calculated if the coefficient for plane waves is known for all angles of incidence between 0 and $\pi/2$. In the case of certain porous substances the reverberation coefficient can be found if the acoustical admittance per unit area is known. It is shown that in general the reverberation coefficient differs from the coefficient at normal incidence. Some numerical values for an ideal porous substance are given by way of illustrating the results obtained.

Biggin Hill, Kent,
November 1927.

LI. *A Theory of Light-Scattering in Liquids.*

By Prof. C. V. Raman, *F.R.S.*, *and* K. S. Krishnan *.

1. *Introduction.*

THE theory of light-scattering in gases with optically anisotropic molecules was discussed by the late Lord Rayleigh † and by Born ‡, whose investigations showed that the anisotropy results in the transversely scattered light becoming imperfectly polarized and also in making its intensity greater than for a gas of equal refractivity with isotropic molecules. In a monograph § by one of us, published in February 1922, and in further papers communicated shortly afterwards to the Philosophical Magazine ||, the case of dense fluids was dealt with, and it was shown that by considering the scattering due to the thermal fluctuations of density in the fluid and also the additional scattering due to the anisotropy and varying orientations of the molecules, the observed phenomena could be satisfactorily explained. A general theory of light-scattering in fluids from the molecular standpoint was worked out shortly afterwards in two papers by Dr. K. R. Ramanathan ¶. His treatment is very wide in its scope and is applicable equally to the case of polar and non-polar molecules. Dr. Ramanathan has returned again to the subject, and in a recent paper ** has examined critically the relation of his general theory to the special treatment worked out by R. Gans †† for the restricted class of liquids with non-polar molecules.

An examination of the data for depolarization of the light scattered by fluids with the aid of Ramanathan's formulæ indicates an apparent change (usually a large diminution) in the optical anisotropy of the molecules of a given substance as it passes from the condition of vapour to that of liquid ‡‡. A similar discrepancy becomes apparent when the optical anisotropy of the molecule is determined from the

* Communicated by the Authors.

† Lord Rayleigh, Phil. Mag. vol. xxxv. p. 373 (1918).

‡ M. Born, *Deutsch. Phys. Gesell. Ver.* vol. xix. p. 243 (1917).

§ C. V. Raman, 'Molecular Diffraction of Light,' Calcutta Univ. Press (1922).

|| C. V. Raman and K. R. Ramanathan, Phil. Mag. vol. xlv. p. 113 (1923); C. V. Raman and K. S. Rao, vol. xlv. p. 625 (1922).

¶ K. R. Ramanathan, Proc. Ind. Assoc. Cult. Sc. vol. viii. pp. 1 & 181 (1923).

** K. R. Ramanathan, Indian Journal of Physics, i. p. 413 (1927).

†† R. Gans, *Zeits. für Physik*, xvii. p. 353 (1923).

‡‡ K. S. Krishnan, Proc. Ind. Assoc. Cult. Sc. ix. p. 251 (1926).

electric double refraction in the liquid *, using the well-known formula due to Langevin, and is compared with the value derived from observations on light-scattering in the vapour. As an explanation of this phenomenon it may of course be suggested that some kind of temporary grouping or association of neighbouring molecules occurs in the liquid in such a manner as to diminish their effective optical anisotropy. Such an assumption however, besides being artificial and qualitative, would appear difficult to sustain, particularly when it is noticed that the apparent diminution of optical anisotropy is quite as marked in liquids usually considered as "non-associated," *e. g.* the paraffins, as in others which are typically "associated" like the alcohols. The facts stated above necessitate a revision of the theory of light-scattering in liquids. It is proposed in this paper to put forward a theory which does not involve any artificial hypotheses and which offers a natural explanation of the observed facts.

2. *The Fundamental Postulates.*

Any satisfactory theory of our subject must consider the optical properties of the molecules composing the fluid, their distribution and orientations in space, and the field actually acting on them. We assume that the molecules are polarizable differently along three mutually perpendicular directions fixed to them, which might be called the principal optic axes of the molecules. As to their distribution and orientations in space, we have not at present full knowledge. The molecular aggregation in liquids is presumably intermediate in character between the two extreme cases of an ideal crystalline solid and a perfect gas. If we follow an individual molecule in a liquid over a sufficiently long time, it can take up all possible positions and orientations, and thus the conditions approximate to those of a gas. If, however, we consider a molecule in relation to its immediate neighbours, the analogy between the solid and liquid states is closer. We are not justified in treating the space-distribution as random, because the molecules have a finite size, and in the dense assemblage forming a liquid they would naturally restrain each other's freedom of movement to a considerable extent. On the other hand, we shall not be seriously in error if we assume the freedom of orientation of the molecules to be comparatively unrestricted in most liquids. It is true that in many actual cases the molecules

* C. V. Raman and K. S. Krishnan, Phil. Mag. iii. p. 727 (1927).

are highly unsymmetrical in shape, and hence in finding the probability of any particular configuration of neighbouring molecules, both spacing and orientation have to be considered together. Nevertheless, we may regard the effect of molecular collisions as equivalent approximately to a restriction of the possible arrangements of the molecules in space, while their freedom of orientation is retained.

To make our ideas more precise, we may fix our attention on a volume element in the liquid whose linear dimensions are large in comparison with the size of a molecule, and consider the spontaneous fluctuations in the number and orientations of the molecules contained in it. We shall make the following assumptions :—

(1) That the fluctuations in density of the fluid present in an element of volume δv are given by the usual Smoluchowski-Einstein expression

$$\overline{\delta n^2} = \frac{\mathrm{RT}\beta n_0^2}{\mathrm{N}\delta v}, \quad \ldots \ldots \quad (1)$$

where $\overline{\delta n^2}$ is the mean square of the deviation of the number of molecules per unit volume from its mean value n_0, R and N are the gas constant and Avogadro number respectively per gram molecule, β is the isothermal compressibility, and T is the absolute temperature.

(2) That the number of molecules in the volume element having at any instant any given orientation, will be the same as though all the molecules in the volume element were oriented entirely at random, and that fluctuations in orientations are entirely uncorrelated with the fluctuations in density.

3. *The Polarization Field in Liquids.*

We have next to consider the question of the field actually acting on any molecule in the liquid. In a gas this will evidently be the same as the field of the incident light-wave. In a liquid, however, we have also to take into account the field due to the doublets induced in the surrounding molecules. This "polarization field" is usually taken to be $\frac{4\pi}{3}\chi \mathrm{E}$, where χ is the susceptibility of the medium per unit volume and E is the incident field, it being thus tacitly assumed that the polarization field acting on any given molecule is independent of its orientation in the field. This assumption would be valid, only if the molecules surrounding

it were distributed in such a manner as to be equivalent to a spherically symmetrical arrangement of polarizable matter. While this assumption may be justified for molecules at a sufficient distance from the one under consideration, it is not necessarily true in respect of its immediate neighbours. If the shape of a molecule departs greatly from spherical symmetry, it would be incorrect to regard the distribution of polarizable matter immediately surrounding it as completely symmetrical. The polarization field acting on a molecule must thus, in general, vary with its orientation in the external field. To express this "anisotropy" of the polarization field in mathematical language, we choose three mutually perpendicular axes fixed in the molecule such that when the incident field lies along any one of them, the polarization field is also in the same direction, and is given by $p_1\chi\mathrm{E}$, $p_2\chi\mathrm{E}$, or $p_3\chi\mathrm{E}$, where p_1, p_2, p_3 are constants characteristic of the molecule for the given density and temperature of the liquid. It is quite possible to discuss the general case where these axes of the molecule are different from its optic axes. However, for simplicity we may assume that the two sets of axes are coincident in direction.

An important question which arises here is whether the local field acting on a molecule is influenced appreciably by the fluctuations of density and molecular orientation in its immediate neighbourhood. This question has been discussed by Ramanathan in his recent paper, and he has given reasons for assuming that the local field should be regarded as constant. His argument may be modified and expressed in the following way :—The local field arises in part from the external field, and in part from the polarization of the entire medium surrounding the molecule under consideration. If the distribution at any instant, of polarizable matter surrounding the molecule, can be regarded as spherically symmetrical, it can be shown by dividing up the medium into concentric spherical shells that the polarization field acting on the molecule at the centre is unaffected by either a diminution or an increase of density in its immediate neighbourhood. This conclusion remains valid even if there be fluctuations from spherical symmetry in the distribution of polarizable matter round the molecule, for it may be shown that this would give rise to a fluctuation of the polarization field which would be uncorrelated in sign with the local variation of density and may therefore be left out of account. The argument of Ramanathan appears to be correct, and, as we shall show later in the course of the paper, its validity remains substantially unaffected even when, as

in our present treatment, the polarization field acting on a molecule is assumed to vary with its orientation in the external field. We now proceed to modify the treatment of light-scattering given by Ramanathan so as to take the "anisotropy" of the polarization field into account.

4. *Radiation from a given Molecule.*

Let a beam of plane-polarized light be incident in the medium along the x-axis of a system of coordinates xyz fixed in space, the electric vector of the light-wave, equal to E, say, lying along the z-axis. Let us consider a molecule at O radiating under the influence of the light-wave. We choose the optic axes of the molecule as the axes of another coordinate system $\xi\eta\zeta$, of course rigidly fixed to the molecule, their orientation in space being defined with reference to the xyz axes by the usual Eulerian angles θ, ϕ, ψ. Then the cosines of the angles between the different axes are given by the following table

Table I.

	x.	y.	z.
ξ ...	$\alpha_{11} = \cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi$.	$\alpha_{12} = \cos\theta\sin\phi\cos\psi + \cos\phi\sin\psi$.	$\alpha_{13} = -\sin\theta\cos\psi$.
η ...	$\alpha_{21} = -\cos\theta\cos\phi\sin\psi - \sin\phi\cos\psi$	$\alpha_{22} = -\cos\theta\sin\phi\sin\psi + \cos\phi\cos\psi$.	$\alpha_{23} = \sin\theta\sin\psi$.
ζ ...	$\alpha_{31} = \sin\theta\cos\phi$.	$\alpha_{32} = \sin\theta\sin\phi$.	$\alpha_{33} = \cos\theta$.

Now, if A, B, C be the moments induced in a molecule per unit field acting respectively along its three axes, then the actual moments induced in the molecule at O along its axes by the electric vector of the light-wave are

$$\left.\begin{aligned} &\mathrm{AE}(1+p_1\chi)\alpha_{13}, \\ &\mathrm{BE}(1+p_2\chi)\alpha_{23}, \\ \text{and}\quad &\mathrm{CE}(1+p_3\chi)\alpha_{33} \end{aligned}\right\} \quad \ldots\ldots \quad (2)$$

respectively. We may denote these expressions shortly by $\mathrm{A'E}\alpha_{13}$, $\mathrm{A'E}\alpha_{23}$, and $\mathrm{C'E}\alpha_{33}$, where

$$\left.\begin{aligned} \mathrm{A'} &= \mathrm{A}(1+p_1\chi), \\ \mathrm{B'} &= \mathrm{B}(1+p_2\chi), \\ \mathrm{C'} &= \mathrm{C}(1+p_3\chi). \end{aligned}\right\} \quad \ldots\ldots \quad (3)$$

When these moments are resolved along the x-axis, their sum is equal to

$$M_x = E(A'\alpha_{13}\alpha_{11} + B'\alpha_{23}\alpha_{21} + C'\alpha_{33}\alpha_{31}). \quad . \quad . \quad (4)$$

At a large distance d from the molecule measured along the y-axis, *i. e.* transversely to both the direction of vibration and the direction of propagation of the incident light, the amplitude of the x-component in the radiation from the given molecule is obviously equal to

$$\frac{k^2}{d} M_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $$k = \frac{2\pi}{\lambda}.$$

Similarly, the amplitude of the z-component of the radiation from the given molecule will be equal to

$$\frac{k^2}{d} M_z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where M_z is the sum of the resolved components along the z-axis, of the moments induced in the molecule, and is given by

$$M_z = E(A'\alpha_{13}^2 + B'\alpha_{23}^2 + C'\alpha_{33}^2). \quad . \quad . \quad . \quad (7)$$

5. *Orientation Scattering.*

We now imagine the space occupied by the fluid to be divided into a large number of equal volume elements forming the cells of a regular cubic space-lattice. The linear dimensions of the volume element are assumed to be small in comparison with a wave-length, and at the same time large enough to include a great many molecules. The fluctuations in the number and orientations of the molecules in any one element may, in the circumstances, be considered to be independent of the fluctuations in the adjoining ones. At any given instant the radiations from the different molecules in a volume element may be taken to be in the same phase; and in order to get their instantaneous aggregate effect at the point of observation, we have merely to add up the amplitudes due to the individual molecules. Thus, for instance, the amplitude, at any given instant, of the x-component of the radiation from a volume element δv will be given by

$$X = \frac{k^2}{d} \Sigma M_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where Σ denotes summation over all the molecules in δv.

We have next to compound the effects due to the different

volume elements. Since each of these contains a large number of molecules, which, as mentioned in section 2, are oriented at random, the average value of ΣM_x (given by (4)) taken over the different volume elements will be nothing. However, for any single element, ΣM_x will, in general, be finite, being as often positive as negative, its actual value being determined by the chance orientations at the given instant of the molecules present in it. The values of ΣM_x for different volume elements will thus be entirely uncorrelated, and the resultant effect is accordingly obtained by addition of the intensities (represented by the squares of the amplitudes), and not by addition of the amplitudes. Thus the problem reduces to one of finding the average value of the intensity taken over all the volume elements, and will evidently be the same as finding what is called in the theory of probabilities the "expectation" of intensity from a single volume element; *i. e.*, the mean value of the intensity to be expected after a very large number of trials in each of which the number and the orientations of the molecules present in it are rearranged arbitrarily according to the principles of statistical mechanics.

Since, as is evident from (1), the fluctuation of density is very small in comparison with the mean density, we may reasonably assume in the calculation that in the different trials the total number of molecules in the element of volume does not vary, only their orientations varying arbitrarily. The expectation of X^2 from δv will then be given by

$$\overline{X^2} = \frac{k^4}{d^2} \times \text{expectation of } (\Sigma M_x)^2 \text{ from } \delta v,$$

which can easily be shown to be equal to

$$\frac{k^4}{d^2} n_0 \delta v \, \overline{M_x^2}, \qquad \ldots\ldots\ldots \quad (9)$$

where $\overline{M_x^2}$ denotes the average value of M_x^2 taken over all the molecules in the element, *i. e.* over all orientations, and is therefore given by

$$\overline{M_x^2} = \frac{\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi}\int_{\psi=0}^{\psi=2\pi} E^2(A'\alpha_{13}\alpha_{11} + B'\alpha_{23}\alpha_{21} + C'\alpha_{33}\alpha_{31})^2 \sin\theta \, d\theta \, d\phi \, d\psi}{\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi}\int_{\psi=0}^{\psi=2\pi} \sin\theta \, d\theta \, d\phi \, d\psi} \qquad \ldots\ldots \quad (10)$$

$$= E^2 F, \qquad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

where

$$F = \tfrac{1}{30}[(A'-B')^2 + (B'-C')^2 + (C'-A')^2]. \qquad \ldots \quad (12)$$

Then from (9) we get for the intensity of the x-component of the scattering per unit volume

$$I_x = \frac{k^4}{d^2} E^2 n_0 F. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Coming now to the z-component, we may write expression (7) for M_z shortly as

$$M_z = EL, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where

$$L = A'\alpha_{13}^2 + B'\alpha_{23}^2 + C'\alpha_{33}^2. \quad . \quad . \quad . \quad (15)$$

As before, by summing up the amplitudes of the radiations from the individual molecules in δv at any instant, we get for the resultant amplitude

$$Z = \frac{k^2}{d} E \Sigma L, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Σ, as before, denoting summation over all the molecules in δv. For convenience in discussion we can rewrite the expression in the form

$$Z = \frac{k^2}{d} E \left[\Sigma \frac{A' + B' + C'}{3} + \Sigma \left(L - \frac{A' + B' + C'}{3} \right) \right]. \quad . \quad (17)$$

$$= \frac{k^2}{d} E \frac{A' + B' + C'}{3} n \delta v + \frac{k^2}{d} E \Sigma \left(L - \frac{A' + B' + C'}{3} \right). \quad (18)$$

The two terms in (18) may be denoted by Z_1 and Z_2 respectively. We shall in the first place consider the second term Z_2, reserving a discussion of the other term to the next section.

At any instant the average value of $\Sigma \left(L - \frac{A' + B' + C'}{3} \right)$ for the different volume elements can easily be shown to be zero. But as in the previous case its actual value for any single element will be finite, in general, and will be determined wholly by the chance orientations of the molecules in it. Hence, so far as the second term of (18), viz. Z_2, is concerned, we have as before to add up the intensities due to the different volume elements in order to get the total intensity.

Following the same reasoning as in the case of the x-component, we get for the expectation of intensity on account of the second term of expression (18) from a volume element δv

$$\overline{Z_2^2} = \frac{k^4}{d^2} E^2 n_0 \delta v \overline{\left(L - \frac{A' + B' + C'}{3} \right)^2}, \quad . \quad . \quad (19)$$

where the bar over the last factor denotes averaging over

all orientations,

$$= \frac{k^4}{d^2} \mathrm{E}^2 n_0 \delta v \times \tfrac{2}{45} [(\mathrm{A}'-\mathrm{B}')^2 + (\mathrm{B}'-\mathrm{C}')^2 + (\mathrm{C}'-\mathrm{A}')^2]. \quad (20)$$

$$= \frac{k^4}{d^2} \mathrm{E}^2 n_0 \delta v \times \tfrac{4}{3} \mathrm{F}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Thus we get for the intensity of this part of the z-component, scattered per unit volume

$$\mathrm{I}_{z2} = \frac{4}{3} \frac{k^4}{d^2} \mathrm{E}^2 n_0 \mathrm{F}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The expression

$$\mathrm{I}_x + \mathrm{I}_{z2} = \frac{7}{3} \frac{k^4}{d^2} \mathrm{E}^2 n_0 \mathrm{F} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

gives the "orientation" scattering per unit volume. In the special case when $\mathrm{A}' = \mathrm{B}' = \mathrm{C}'$, *i. e.* when the moments induced in a molecule are isotropic, $\mathrm{F} = 0$ and the orientation scattering naturally disappears.

6. *Density Scattering.*

We have still to consider the first term in (18), viz.

$$\mathrm{Z}_1 = \frac{k^2}{d} \mathrm{E} \frac{\mathrm{A}' + \mathrm{B}' + \mathrm{C}'}{3} n \delta v. \quad . \quad . \quad . \quad (24)$$

$\frac{\mathrm{A}' + \mathrm{B}' + \mathrm{C}'}{3}$ is the average moment induced in a molecule per unit external field, the average being taken over all directions of incidence of the field with respect to the molecule. The actual field on the molecule which produces this moment can be divided into three parts :—

(*a*) The external field.
(*b*) The field arising from the doublets outside a spherical volume element containing the molecule at its centre.
(*c*) The field arising from the molecules within the volume element.

For the reasons given in section 3, the fields (*a*) and (*b*) will be unaffected by the fluctuations of density in the volume element, and hence the corresponding contribution from these fields to the mean moment of the molecule, viz.

$$\frac{\mathrm{A} + \mathrm{B} + \mathrm{C}}{3} \left(1 + \frac{4\pi}{3} \chi\right),$$

can be regarded as constant.

The rest of the contribution to the mean moment, viz.

$$\tfrac{1}{3}(A\sigma_1+B\sigma_2+C\sigma_3)\chi, \quad . \quad . \quad . \quad . \quad (25)$$

$$\left.\begin{aligned}\sigma_1&=p_1-\frac{4\pi}{3},\\ \sigma_2&=p_2-\frac{4\pi}{3},\\ \sigma_3&=p_3-\frac{4\pi}{3},\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

comes from field (c) due to the immediate neighbours, and hence will vary directly with the fluctuation of n in the volume element. However, in any actual case $A\sigma_1+B\sigma_2+C\sigma_3$ is negligible in comparison with $A+B+C$ (generally 1 or 2 per cent.), and hence we may reasonably assume that the whole of the mean moment, *i. e.* $\dfrac{A'+B'+C'}{3}$, is independent of the fluctuations of n.

Expression (24) can then be written in the form

$$Z_1=\frac{k^2}{d}E\frac{A'+B'+C'}{3}n_0\delta v+\frac{k^2}{d}E\frac{A'+B'+C'}{3}\delta n\,\delta v. \quad (27)$$

The first term represents that part of the amplitude which will be constant for the different volume elements, and on compounding will cancel each other out by mutual interference, owing to the regularity in the arrangement of the volume elements in the medium. The amplitude represented by the second term, however, being determined by the chance fluctuation δn, will be uncorrelated for the different volume elements, and we shall have to add their squares to get the resultant intensity. Thus

$$\overline{Z_1^2}=\frac{k^4}{d^2}E^2\left(\frac{A'+B'+C'}{3}\right)^2\overline{\delta n^2}\,\delta v^2, \quad . \quad . \quad (28)$$

which, using (1) and the relation

$$n_0\frac{A'+B'+C'}{3}=\frac{\mu^2-1}{4\pi}, \quad . \quad . \quad . \quad . \quad (29)$$

where μ is the refractive index of the medium, reduces to

$$\overline{Z_1^2}=\frac{k^4}{d^2}E^2\frac{RT\beta}{N}\left(\frac{\mu^2-1}{4\pi}\right)^2\delta v. \quad . \quad . \quad . \quad (30)$$

Thus we have for the "density scattering" per unit volume

$$I_{z1}=\frac{k^4}{d^2}E^2\frac{RT\beta}{N}\left(\frac{\mu^2-1}{4\pi}\right)^2. \quad . \quad . \quad . \quad . \quad (31)$$

The total intensity of the z-component

$$I_z = I_{z1} + I_{z2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where I_{z1} and I_{z2} are given by (31) and (22) respectively.

7. *Depolarization and Intensity of the Scattered Light.*

If the incident light travelling along Ox is unpolarized, we shall have to take into consideration also the y-component of the primary vibrations, which, being along the direction of observation, will contribute equally to the intensities of the x- and z-components of the transversely scattered light, an amount given by (13).

Thus in this case the intensity of the x-component will be equal to $2I_x$ and that of the z-component to $I_z + I_x$, and the ratio of the components is given by

$$r = \frac{2I_x}{I_z + I_x} = \frac{2n_0F}{\frac{RT\beta}{N}\left(\frac{\mu^2-1}{4\pi}\right)^2 + \frac{7}{3}n_0F} \quad . \quad . \quad . \quad . \quad (33)$$

Also the total intensity of the transversely scattered light expressed in terms of the incident intensity $I_0 = 2E^2$, becomes

$$I = I_0 \frac{\pi^2}{2d^2} \frac{RT\beta}{N\lambda^4} (\mu^2-1)^2 \frac{6+6r}{6-7r} \quad . \quad . \quad . \quad (34)$$

In the special case when the polarization field is isotropic,

$$p_1 = p_2 = p_3 = \frac{4\pi}{3}$$

and

$$F = \tfrac{1}{30}[(A-B)^2 + (B-C)^2 + (C-A)^2]\left(1 + \frac{4\pi}{3}\chi\right)^2$$

$$= \tfrac{1}{30}[(A-B)^2 + (B-C)^2 + (C-A)^2]\left(\frac{\mu^2+2}{3}\right)^2, \quad (35)$$

and the expressions r and I reduce naturally to those obtained recently by Ramanathan.

8. *Comparison with Experiment:* (a) *Intensity.*

We now proceed to consider how far the above expressions are in conformity with actual experimental results. First we take up the intensity of the transversely-scattered light. From a critical examination of the available data, it has

been shown by one of us * that relative measurements of intensity in a large number of organic liquids entirely support expression (34). We reproduce here the calculations for some typical cases for which we have accurate values for the compressibility from the measurements of Tyrer †.

TABLE II.

Liquid.	r (observed).	I (relative to ether=1) at 30° C.	
		Calculated according to (34).	Observed.
Water	0·085	0·19	0·19
Methyl alcohol	0·060	0·51	0·56
Ethyl alcohol	0·053	0·58	0·57
Ethyl acetate	0·230	0·95	0·98
Carbon tetrachloride	0·053	0·96	1·02
Chloroform	0·240	1·31	1·26
Acetic acid	0·455	1·39	1·42
Ethylene chloride	0·36	1·40	1·44
Ethyl bromide	0·250	1·55	1·58
Benzene	0·47	3·13	3·2
Toluene	0·51	3·29	3·4
Aniline	0·60	3·59	3·42
Meta xylene	0·57	3·90	3·87
Chlorobenzene	0·58	4·09	4·10
Nitrobenzene	0·74	7·6	10·5
Carbon bisulphide	0·64 0·685	10·9 14·1	12·9

Thus over the whole range of intensities from 0·2 to 13, relative to ether, the agreement between the observed and calculated values is very satisfactory. Nitrobenzene is the only exception, the discrepancy being too large to be attributable to error of measurement. However, since it shows a very high depolarization (the highest in the list), any impurity present in the liquid is likely to lower the observed value of r and consequently the calculated value of I considerably; whereas the actual intensity will be

* K. S. Krishnan, Proc. Ind. Assoc. Cult. Sc. ix. p. 251 (1926).
† D. Tyrer, Journ. Chem. Soc. cv. p. 2534 (1914).

increased. Further it is a coloured liquid. It would be of interest to repeat the measurement with a specially purified specimen.

Recently in the authors' laboratory, Mr. Ramachandra Rao * has studied the scattering by six typical organic liquids over a wide range of temperature up to the critical point. The relative values of the intensity at different temperatures again confirm the validity of the above expression for I.

Absolute measurements of intensity available also support expression (34), as will be evident from Table III. $\frac{I}{I_0}d^2$ gives, according to our notation, the fraction of the incident unpolarized light scattered transversely per unit volume of the liquid, per unit solid angle.

TABLE III.

Liquid.	λ in A.U.	Temperature ° C.	r.	$\frac{I}{I_0}d^2\times10^6$. Calculated according to (34).	$\frac{I}{I_0}d^2\times10^6$. Observed.	Observer.
Ethyl ether..	4358	20	0·080	8·85	9·2	Martin & Lehrman †.
Benzene	5440	15	0·41	8·85	$10\cdot7\pm0\cdot55$	Cabannes & Daure ‡.
			0·47	10·7		

9. *Comparison with Experiment:* (b) *Depolarization.*

Expression (33) enables us to determine the depolarization of the light scattered by a fluid in terms of A, B, C, the optical constants of the molecule and p_1, p_2, p_3, the constants of anisotropy of the polarization field. In the case of a rarefied fluid, the polarization field is very small and may be neglected. For a dense fluid, if we disregard the "anisotropy" of the field and assume that

$$p_1=p_2=p_3=\frac{4\pi}{3},$$

* S. Ramachandra Rao, Indian Journal of Physics, ii. p. 7 (1927).

† W. H. Martin and S. Lehrman, Journ. Phys. Chem. xxiv. p. 478 (1920).

‡ J. Cabannes and P. Daure, *Comptes Rendus*, clxxxiv. p. 520 (1927).

then the depolarizations in the liquid and gaseous states are connected by the simple relation

$$\frac{RT\beta}{N} n_0 \cdot \frac{r_{liq.}}{6-7r_{liq.}} = \frac{r_{gas}}{6-7r_{gas}}. \quad . \quad . \quad . \quad (36)$$

The value of $r_{liq.}$ calculated from expression (36) usually, however, differs widely from the observed value. In the case of the carbon compounds, the differences are very marked in the case of the paraffins and the monohydric alcohols, the observed depolarization being much smaller than the calculated value; the differences are less conspicuous in the aromatic series of compounds.

A natural explanation of these facts is furnished by taking into account the anisotropy of the polarization field. It is sufficient as an illustration to consider the cases of the paraffin series of hydrocarbons. As is well-known from chemical considerations and from X-ray data, the molecules of these compounds form elongated chains of carbon atoms, to which the hydrogens are linked. The length of the chain is much greater than its cross-section. X-ray study of the liquid shows, as might be expected *a priori*, that the molecules lie much more frequently touching one another side to side and much less frequently end to end. In these circumstances it would obviously be incorrect to assume the polarization field acting on a molecule to be independent of its orientation in the field. A much closer approximation to the truth is to consider the molecule as equivalent to a doublet placed at the centre of a prolate ellipsoidal cavity scooped out of a continuous isotropic medium, the dimensions of the cavity being determined by those of the molecule. The values of p_1, p_2, p_3 are readily calculated from the expressions

$$p_1 = 4\pi\left(\frac{1}{e^2}-1\right)\left(\frac{1}{2e}\log\frac{1+e}{1-e}-1\right), \quad . \quad . \quad (37)$$

$$p_2 = p_3 = 2\pi\left(\frac{1}{e^2}-\frac{1-e^2}{2e^3}\log\frac{1+e}{1-e}\right), \quad . \quad . \quad (38)$$

where e is given by

$$b = c = \sqrt{1-e^2}\,.\,a, \quad . \quad . \quad . \quad . \quad . \quad (39)$$

a, b, c being the axes of the cavity.

In Table IV. are given the values of the depolarization factor computed in this way, and those observed are tabulated for comparison. A satisfactory agreement is indicated.

TABLE IV.

All the quantities refer to 30° C.

Substance.	Dimensions of the molecule in A.U.		$r_{gas.}$	$r_{liq.}$ calculated from		$r_{liq.}$ observed.
	$a.$	$b=c.$		(36). (Isotropic polarization field).	(33). (Anisotropic polarization field).	
Pentane ...	8·7	4·9	0·0136	0·21	0·074	0·075
Hexane ...	10·0	,,	0·015	0·31	0·087	0·100
Heptane...	11·3	,,	0·0158	0·38	0·083	0·127 0·100
Octane ...	12·6	,,	0·0186	0·46	0·105	0·129

10. *Summary.*

An examination of the data for the depolarization of the light scattered by fluids, with the aid of the molecular theory due to Ramanathan, indicates an apparent change, usually a large diminution, in the optical anisotropy of the molecules of a given substance, as it passes from the condition of vapour to that of liquid. In the present paper a new theory is put forward which offers a natural explanation of the foregoing fact without any artificial hypotheses. In the treatment of the optical properties of liquids usually given, the polarization field acting on a molecule is assumed to be independent of its orientation in the field. This assumption is not justifiable when the shape of the molecule departs greatly from spherical symmetry, and consequently the distribution of polarizable matter surrounding it ceases to be symmetrical. The strength of the polarization field will in these circumstances be dependent on the orientation of the molecule in the field, and may be expressed in terms of three constants characteristic of the molecule for the given density and temperature of the fluid. The theory of light-scattering is developed on this basis, and gives an expression for the intensity of scattering which is in close accord with facts. It also enables the depolarization of the scattered light in the liquid to be successfully calculated from that of the corresponding vapour, at least in those cases where the constants of anisotropy of the polarization field can be determined from the shape of the molecule.

210 Bowbazar Street,
Calcutta, India.
18th August, 1927.

LII. *The Influence of Charged Metallic Points on the Spark Discharge.* *By* JOHN THOMSON, *M.A., B.Sc., Houldsworth Research Student in the University of Glasgow* *.

THE well-known action of a sharp metallic point in facilitating the passage of a spark across a gap near which it is placed has recently been the subject of two papers, the main object of which was the elucidation and explanation of the effect. In the first of these, by C. E. Wynn-Williams †, a number of experiments are described which led the author to the conclusion that the effect is mainly due to the ionization of the air in the gap by a radiation proceeding from the metallic point, and that the properties of the radiation are identical with those of the Entladungstrahlen discovered by E. Wiedemann in 1895. The second paper is by J. D. Morgan ‡, whose experiments support the conclusions arrived at by Wynn-Williams, but are claimed to indicate also that the radiation emanating from the metallic point is effective only when the potential of the point is transitory, and that when the point is subjected to a steady potential (as by a Wimshurst machine) the effect on the spark is due, not to electromagnetic radiation, but to a streaming of ions from the point to the gap.

The experiments to be described in the present communication were initiated for the purpose of further investigating the source and properties of the radiation referred to; they have, however, also led the present writer to a rather different explanation of the action of the charged metallic point.

Experimental Arrangements.

It will be well here to refer briefly to the principal arrangements of the spark-gap and metallic point which were used in the experiments to which reference has just been made. Fig. 1 *a* shows the arrangement known as the "three-point gap," in which A, B are the main spark-gap electrodes, and C an insulated metal rod the point of which is placed very near one of the main electrodes. The effect is produced only when small sparks pass between C and the main electrode adjacent to it. In this arrangement the rod C need not be very sharply pointed; a blunt point is almost equally effective.

* Communicated by Prof. E. Taylor Jones, D.Sc.

† C. E. Wynn-Williams, Phil. Mag. vol. i. p. 353 (1926).

‡ J. D. Morgan, Phil. Mag. vol. iv. p. 91 (1927).

In fig. 1 *b* is shown an arrangement in which the rod C is connected to one of the main electrodes. This is the arrangement used by Wynn-Williams in most of his experiments. The end of C need not be very near one of the main electrodes, but it must be very sharply pointed to produce the effect on the main gap. In this case the radiation is believed to originate in the silent discharge at the sharp point of C.

Fig. 1 *a*.

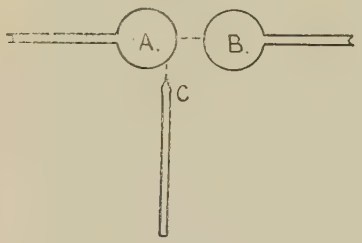


Fig. 1 *b*.

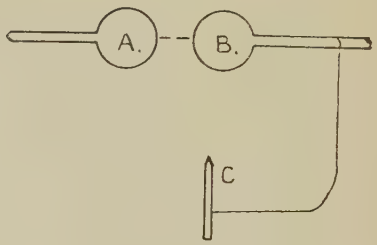


Fig. 1 *c*.

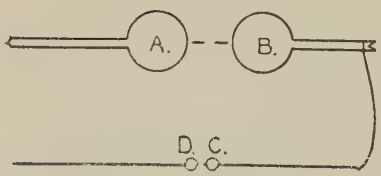


Fig. 1 *d*.

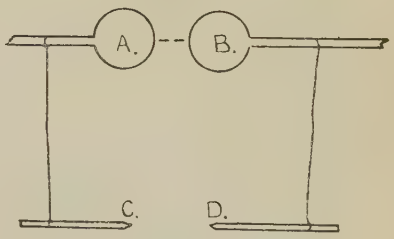


Fig. 1 *e*.

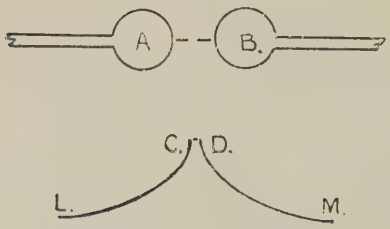
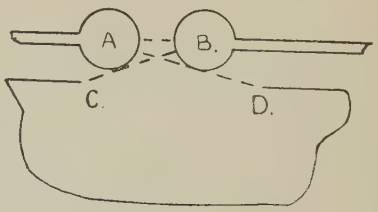


Fig. 1 *f*.



Another arrangement used by Wynn-Williams is shown in fig. 1 *c*. The pointed third electrode is replaced by a small metal sphere connected to one of the main electrodes and held near another small sphere D attached to the end of an insulated wire. The small spark passing between C and D was found by Wynn-Williams to give rise to ionizing radiations similar in their properties to those proceeding from the silent discharge from C in fig. 1 *b*.

The Spark-gaps employed in the Present Experiments.

The present writer has found that, in addition to the arrangements of gap and auxiliary conductors described in the previous section, there are a number of other systems in which similar effects are produced. Some of these are shown in fig. 1. Fig. 1 *d* shows a symmetrical arrangement in which two sharp needles, C, D, are connected to the main electrodes. If the distance between the points C and D is just great enough to prevent a spark from passing between them, the effect on the main gap is very marked if the distance between AB and CD is not more than 10 cm. (AB was 1 cm.). Another symmetrical arrangement is shown in fig. 1 *e*, in which a very small spark passing between C and D, the adjacent ends of insulated wires, takes the place of the silent discharge. This arrangement is also very effective up to the distance of 4 cm. between AB and CD. If the ends L, M are joined by a copper wire, the effect is still found if the small auxiliary gap CD is within 1 cm. of A or B. In fig. 1 *f* C and D are the points of two needles the outer ends of which are connected by a copper wire, but which are otherwise insulated. In this arrangement the effect on the main gap is very marked, even though no sparks pass between A and C or between B and D.

The Source of the Radiations.

With the arrangement of fig. 1 *d* a series of experiments was made with the object of determining the exact source of the radiations. The potential applied to the main gap (generated by an induction coil with motor mercury jet interrupter) being adjusted so that sparks just failed to appear, a thin plate of paraffin wax having a narrow aperture was placed between AB and CD, and moved about until the effect on the passage of the spark was greatest. In this way it was found that practically the whole of the effect originated in the immediate neighbourhood of one or other of the points C, D. The effect was most marked when the aperture allowed a straight path in air from the positive point to the point A of the negative electrode (fig. 2). This result was confirmed by attaching a narrow tube of the same material to the wax plate, as shown in fig. 2, in order to limit the radiation to a still narrower pencil. The most favourable position of the shield is shown in the figure. With this arrangement the greatest distance, AC, at which the effect could be produced was 8 cm., the width of the main gap,

AB, being as usual 10 mm. If the shield was so placed that the pencil failed to strike either of the main electrodes, but passed directly between them, the effect on the main gap was much weaker, being only observable when the distance AC was not more than 4 cm. In another experiment one of the main electrodes, A, was covered with a thin layer of paraffin wax except at the point nearest the other electrode.

Fig. 2.

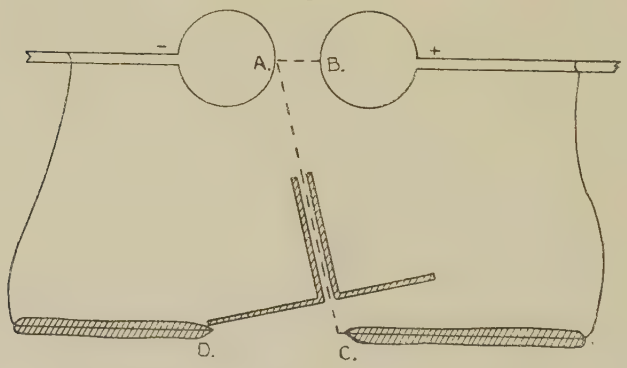
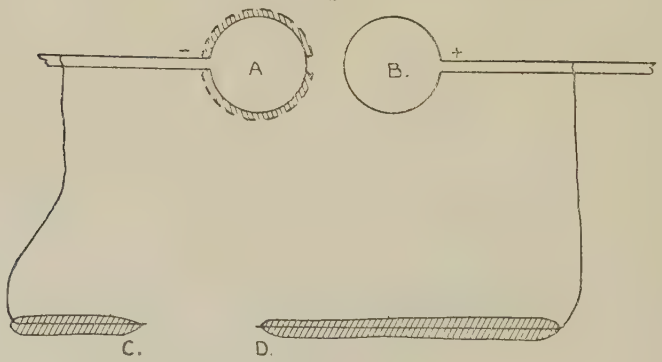


Fig. 3.



The auxiliary gap, CD, was then moved to one side as shown in fig. 3, so that no radiation could pass directly from C or D on to the uncovered part of A. With this system the effect on the main gap was much more marked when B and D were negative than when they were positive.

Practically identical results were obtained when the aperture in the wax shield was covered with a thin film of celluloid. This indicates that the effect on the main gap is caused by electromagnetic radiation, since it is highly

improbable that positive or negative ions can penetrate such a film in the conditions of the present experiments. Such penetration would be likely to occur only if the charged particles were *projected* with high velocity from the points, but in other experiments strong evidence was found (as will be seen later) against this supposition.

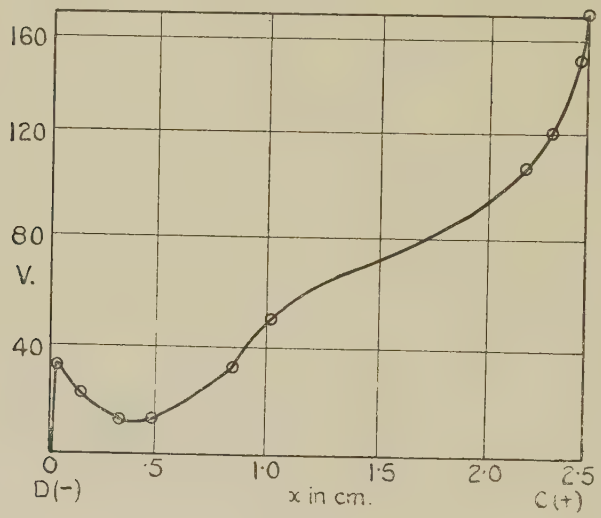
On the whole this series of experiments strongly suggests that, while a small effect arises from a radiation which ionizes the air in the main gap, a much greater part of the effect is photo-electric in character, arising probably from ultra-violet radiation proceeding from the neighbourhood of the positive point. This conclusion seems to be borne out by the fact that the effect of the metallic point in facilitating the discharge at the main gap is very much less marked if the electrodes of the latter are dirty or oxidized. It may be remarked that results practically identical with those just described were found when either of the main spark electrodes was earthed.

With the arrangement of fig. 2, in which a very narrow directing tube was attached to the wax shield, a series of observations was made with the object of determining more exactly the source or sources of the radiation. First the tube was placed so as to be in line with the point A and various points in the line CD, thus examining the relative intensities of the photo-electric radiation from different parts of the discharge. The radiation was found to be much more intense at the positive than at the negative point, while an important conclusion was that, in order to obtain the effect to a marked degree, it is not necessary that C or D should be in line with the point A. The air near C or D is almost equally effective, and an appreciable effect is produced by points in the air at 2 mm. from C or D. Similar experiments in which the main electrodes were shielded allowed the source of the ionizing radiation to be investigated. The effect due to ionization appears to be of almost equal intensity whether it proceeds from the neighbourhood of the positive or the negative point. Again, the air near the point seems to be the source of the radiation.

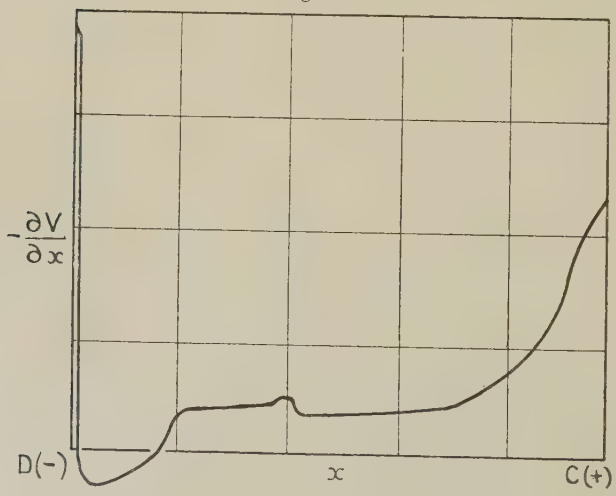
For comparison with these results a series of measurements was made of the potential at various points in the auxiliary gap CD. For this purpose a water-dropping collector, consisting of a fine glass capillary tube, was placed just above the line CD, so that water fed into it broke into drops in this line. The water was connected to one terminal of a Kelvin vertical voltmeter, the other terminal of the instrument being connected to D. The reading on the voltmeter indicated the R.M.S. voltage between D and the collector.

The results of these experiments are shown in fig. 4, the ordinate representing the R.M.S. potential difference between D and various points of the gap CD. The derivative curve,

Fig. 4.



Fiig. 5.



representing the potential gradient along CD, is shown in fig. 5. A comparison of these curves with the results obtained for the intensity of the radiations across the source CD shows that the most effective part of the source is not

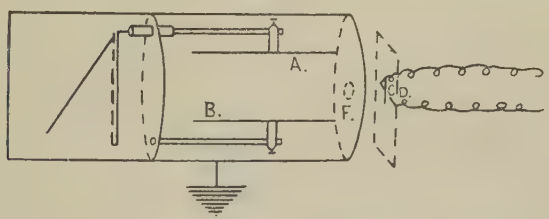
that part where the electric force is greatest, but the part where the positive potential is greatest.

The electric force is greatest near the negative point D (cathode fall), and, on the assumption that the radiations are generated by the impact of ions on air molecules, it is to be expected, according to the quantum theory, that the radiation of greatest frequency will be generated near D. If V is the fall of potential in a very short distance (comparable with the mean free path of the electron in air at atmospheric pressure), the frequency is given by the quantum relation $h\nu = Ve$. It seems probable therefore that the radiation which produces the effect on the main gap is not the radiation of greatest frequency. The most effective portion is that which originates in the region of highest positive potential near C.

Experiments with an Ionization Chamber.

In order to obtain further information as to the properties of the radiations, the main gap AB was removed and replaced

Fig. 6.



by an ionization chamber containing two parallel metal plates, A, B, one of which, A, was insulated and connected to an ordinary gold-leaf electroscope. The other plate, B, was at first connected to the wall of the chamber. The arrangement is shown in fig. 6. The point gap, CD, connected to the induction coil, was placed horizontally in front of the chamber and 2 cm. from it, and by means of the slotted shield the radiation from C or D could be allowed to enter the chamber through the aperture F. C was the positive and D the negative point. The upper plate A, and consequently the electroscope, was charged to about $+600$ or -600 volts, and the rate of discharge was observed with C or D opposite the slot. The numbers given in the table below indicate the angular movement of the gold-leaf in a fixed time (about 10 seconds), and are assumed

to be proportional to the currents flowing to or from A. The normal leakage of the electroscope in 10 seconds was quite negligible. The rate of discharge of the electroscope was comparable with the normal leak when points between C and D were opposite the slot.

Potential of A.	Point Source.	Current to A.
+600	C	7
−600	C	120
+600	D	550
−600	D	19

These results clearly indicate that the current to the plate A is not due to ionization of the air between A and B alone, since in that case the first two results in the table would be equal and also the last two. To investigate this further, a Wilson tilted electroscope was substituted for the ordinary electroscope and the following series of experiments was carried out:—The earthed plate B of the ionization chamber was replaced by a similar insulated plate which could be charged to any desired potential, while the plate A was connected to the leaf of the tilted electroscope. The aperture F was covered with gauze connected to the earthed walls of the chamber in order to eliminate inductive effects on A due to the charges at the point gap. The electroscope was found to be sufficiently sensitive with the attracting plate charged to a potential (with respect to the earth) of ± 210 volts, the leaf system and plate A to ± 25 volts, and the instrument tilted to about 30°. The case of the electroscope was of course earthed, and the point gap with shield was arranged as in the former experiment.

(*a*) The plate A was charged to +25 volts, the electrode D (negative) being placed opposite the aperture. Plate B was charged to various potentials, V_B. The rate of discharge of the electroscope was found to vary as V_B was varied; the graph of the results is shown in fig. 7, curve *a*. The ordinate represents the rate of discharge of A, the abscissa the potential V_B.

(*b*) In the next experiment the plate A was charged to −25 volts, and electrode C (positive) was placed opposite the aperture. The relation between the rate of discharge of A and V_B is shown in fig. 7, curve *b*.

In order to interpret these results it may be supposed that

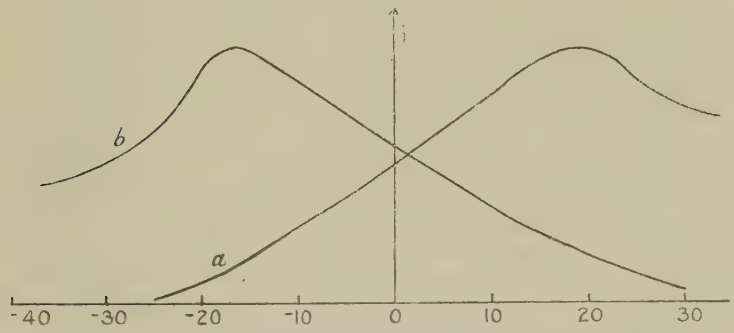
there are three conceivable ways in which the point C or D might cause discharge of the electrode A, viz. :—

(i.) By the emission of an electromagnetic radiation which ionizes the air between A and B.

(ii.) By the emission of ions of the same sign as the point, projected with a comparatively large velocity through the air between A and B.

(iii.) By the production of ions in the vicinity of the aperture F, but not in the space between the plates A and B.

Fig. 7.



(i.) According to the first hypothesis, the current from A to B should clearly be zero when A and B are at the same potential, and as the difference between V_A and V_B increases, the current should steadily increase, *i. e.* the current varies with $\pm(V_A - V_B)$.

(ii.) In this case also the current would be due to the electric field between A and B. If the projected ions did not ionize the air through which they passed, then the current would increase as the negative potential of B increased. If the projected ions ionized the air, then this case would reduce to (i.), and the current would vary as in that case.

(iii.) On the third hypothesis the current to A would depend entirely on the electric field between the edge of the electrode A and the earthed gauze over the aperture. A consideration of the distribution of electric charge in the system within the ionization chamber leads to the conclusion that the gauze will have a very small charge when the potentials of the plates A and B are equal but opposite. On the other hand, when A and B are charged to the same potential, the induced charge on the gauze is very much greater. Since tubes of electric force originate in charges

on conductors, and since the electric force in the vicinity of a conductor is measured by the number of tubes of force per unit area originating on it, it is concluded that the force between the plate A and the gauze F is very much greater when A and B are at the same potential than when they are at equal but opposite potentials. Consequently it is to be expected that a much greater current of ions will move from the gauze to either plate when they are at the same potential than when they are at opposite potentials.

Another way of looking at the same problem is to consider extreme cases of the potential V_B. If V_B is very large and of the opposite sign to V_A, then the potential near the gauze F will be of the same sign as potential V_B. Consequently ions of this sign will be repelled to the gauze, and none will reach the plate A. Now the current measured was the current to A, and this was due to ions of the opposite sign to V_A. Therefore, if V_B is large and of the opposite sign from V_A, no current will be obtained. As the potential of the plate B approaches that of the plate A, there will come a time when a fairly large current of ions will move towards A. Then if V_B is very large and of the same sign as V_A, although ions will be attracted in large numbers from the gauze into the chamber, they will almost all find their way to the plate B, since the field of force between A and B will tend to drive them towards B. Thus, again, when V_B is very large, a very small current will be obtained. This indicates that a maximum current will occur when V_B is somewhere near to V_A.

The curves of fig. 7 obtained experimentally agree very well with this hypothesis, and accordingly it is concluded that the ions produced by the discharge do not reach the air between A and B, unless they are assisted by the action of an electric field. It is thus possible to put a limit to the distance from the discharge at which ions are *produced*. This limit as shown by these experiments is about 3 cm.

Similar experiments with A negatively electrified and D opposite the aperture, or with A positively electrified and C opposite, led again to the curves of fig. 7. Now, since in this case the ions causing the current were of opposite sign to the point source, this experiment shows that both kinds of ions are produced by the influence of each point.

In order to test the matter further, the following experiment was tried. The earthed wire gauze across the aperture F was replaced by an insulated piece of gauze which could be charged to various potentials. With A at

+ 25 volts, and B at + 20 volts, it was found that the current to A varied almost directly as the field from the gauze to A, the current increasing as the negative potential of the gauze increased. Similarly, with A charged to − 25 volts and B to − 16 volts, the current from A increased as the positive potential of the gauze increased. No current could be observed in either case if the gauze and A were at the same potential, or if the distance of C or D from the gauze was more than 3 cm. These experiments also support the hypothesis that the ions are produced near the gauze, but not in the space well between the plates A and B.

Another experiment was arranged to determine roughly the relative number of ions present at various distances from the source of the radiation. For this purpose a strong electric field was required, and therefore the tilted electroscope was replaced by the upright type, which could be used at potentials of about 600 volts relative to the case, which was earthed. The gauze was removed from the aperture F (fig. 6), and the point gap was arranged so that it could be moved in a direction perpendicular to itself and the face of the ionization chamber. This allowed the distance x from F to CD to be varied and to be accurately measured. The experiment consisted in observing the rate of discharge of the electroscope for different values of x, which was varied from 4 cm. to 6 cm. In all cases the relation between the rate of discharge and x was found to be represented by an exponential expression of the form $i = i_0 e^{-kx}$, where i is the rate of discharge of the electroscope and i_0 is some constant.

The exponential decrease in the current must now be explained on the assumption that no ions are *produced* at distances greater than 3 cm. from the discharge. Since ions *did* reach the chamber, there must be a field of force between the place where the ions are formed and the aperture F. This is not surprising when the high potential of the plate A is considered. This plate (positive) will attract negative and repel positive ions, so that the current flowing from the vicinity of the discharge to the aperture will consist entirely of negative ions. Let this current at any point be i across unit cross-section, and let the current at the point beyond which no ions are formed (3 cm. from the discharge) be i_0. The decrease in the current must be due to some form of diffusion of the ions. No recombination occurs, since there are assumed to be no positive ions present. This diffusion is principally due to the mutual repulsion of the ions, causing them to move away from one another.

Consequently the decrease in the current, i, will be proportional to the number of ions present, or, if the flow of ions is being considered, will be proportional to the current itself. Thus, if k is the fraction of the current lost along 1 cm. of the distance x, the increase in the current across an element dx will be represented by the quantity $-kidx$. That is,

$$di = -ki\,dx,$$

giving $$i = i_0 e^{-kx}.$$

It is to be noted that this diffusion is not the same as that occurring when ions of one sign are present in a closed chamber. There the diffusion current is due to the absorption of ions near the surface of the chamber; the expression representing such diffusion is entirely different.

There now remains to be investigated the question of how these ions are produced by the action of the point discharge. The experiments made with the spark gap indicate that ionizing radiations emanate from the vicinity of the point. None of the experiments described above have given any evidence to contradict this view. On the other hand, they have established that the production of the ions is brought about either by fast-moving ions, projected from the points and capable by reason of their velocity of ionizing air, or by an electromagnetic radiation. They have also shown that in either case the ionization ceases at a distance of about 3 cm. from the gap.

Again the tilted electroscope was employed, and the aperture F was screened by an earthed wire gauze. In this experiment, however, the aperture was also covered by a thin film of celluloid similar to that used in the spark-discharge investigations. The electrode B was earthed, and the point gap was about 1 cm. from the aperture F. Observations were taken of the rate of discharge of A. In this case the normal leakage of the electroscope had to be measured and deducted. The readings varied considerably with the intensity of the field across the gap CD, a typical result being given in the following table :—

Potential of A in volts.	Source.	Rate of discharge of A.
+25	Positive point.	6
+25	Negative point.	4
−25	Positive point.	6
−25	Negative point.	4

In each experiment the ratio of the rates of discharge of plate A due to C and D did not vary when the potential

of A was changed from −25 to +25 volts. This means that whatever emanates from the point and penetrates the celluloid produces equal numbers of positive and negative ions. That is, in this case true ionization of the air in the chamber is taking place, either by the action of a radiation or by the impact of high-velocity ions on air molecules. It is highly improbable that anything of the nature of cathode or positive rays is given off by a point discharge in air at atmospheric pressure, and ions of smaller velocities than these would be stopped (or at least lose their ionizing speed) by the impact with the celluloid film. Moreover, the previous experiments have shown that ionization does not take place at distances greater than 3 cm. from the discharge ; material particles brought to rest by 3 cm. of air would certainly be unable to penetrate the film. The conclusion is therefore that the ionization is caused by an electromagnetic radiation.

Another point to be noted is that the experiment did not allow any photo-electric radiation which might be present to be detected, since the electrodes A and B were not in a direct line from C or D. The numbers given are therefore measures of the relative intensities of the ionizing radiations from the two points, as detected at 3 cm. distance from their sources. It cannot be stated, however, that the relative intensities at the sources are in the same ratio, as that assumes that the radiations from the two points are of the same average wave-length or "hardness."

The next experiment was intended to detect and measure the photo-electric radiations which were suspected to be present. The plate B was removed and A was replaced by a clean zinc plate Z, facing the aperture F and about 1 mm. from the wire gauze. Thus radiations from the point acting as source actually fell on the zinc plate, whereas in the previous experiments they did not fall on *any* metal surface inside the chamber. The aperture was again covered by a celluloid film. The usual measurements of the rate of discharge of the plate Z were taken with the positive point C and then with the negative point D as source. The results are shown below.

Potential of Z in volts.	Source.	Rate of discharge of Z.
+25	Positive point.	6
+25	Negative point.	4
−25	Positive point.	24
−25	Negative point.	4

The results with Z positive are a repetition of the results in the previous experiment. Since there is no photo-electric

effect with Z charged to +25 volts, the numbers represent the relative intensities of the ionizing radiations at 3 cm. from their sources, thus confirming the results already obtained. With Z negative, however, the results are different. The rate of discharge with the negative point as source is as before, showing that little or no photo-electric radiation emanates from it; but the rate of discharge with the positive point as source is about four times as great as before. This indicates a strong photo-electric effect due to radiations from the neighbourhood of the positive point. It also shows that the ionizing effect of the radiations is much less powerful than the photo-electric effect, confirming the results obtained with the spark discharge. It is possible and in fact probable that some photo-electric radiation emanates from the vicinity of the negative point. Our experiment merely indicates that its intensity must be less than one-twentieth of the intensity of the similar radiation from the positive point. So far, direct experiment has given no indication as to whether the photo-electric effect is produced by the radiation responsible for the ionization effect or by one of different wave-length. The spark-discharge experiments, however, showed that a photo-electric effect could be produced at the gap when the source of the radiation was (under favourable circumstances) 15 cm distant. The ionizing radiation under no circumstances will penetrate more than 3 cm. of air. Consequently it may be said that whether the ionizing radiation can or cannot produce the photo-electric effect, other radiations are present whose absorption by air is smaller and which are photo-electric.

It is well known that the photo-electric emissivity of a metal is a function of the wave-length of the incident radiation. The maximum emission is due to radiation of a certain fixed wave-length. It is also known that the wave-length corresponding to the maximum emissivity varies from metal to metal; in general the more electro-positive metals respond to longer wave-lengths, and the more electro-negative to shorter wave-lengths. Consequently the experiment just described cannot be said to give any general information with regard to the intensity of the radiations. The results must be taken to refer only to zinc or allied metals.

The experiments just described show that both ionizing and photo-electric radiations are emitted by a point charged to a high positive potential. Photo-electricity is in general associated with radiations of longer wave-lengths than those

which ionize air, and therefore it is reasonable to suppose that the radiations from the point are very heterogeneous in character. A rough spectral analysis might be performed by a series of experiments on the velocities of photo-electrons. With the positive point at a fixed distance from the zinc plate a determination might be made of the minimum wave-length of the incident radiations, by the usual method of measuring the positive potential to which the plate rises. By making similar determinations with different distances between the source and the plate, a curve might be obtained giving the minimum wave-length as a function of this distance. Such a curve would indicate the type of spectrum emanating from the point. It would of course be necessary to see that the ionizing radiations were not allowed to interfere, by using suitable distances (greater than 3 cm.) between the source and the plate, and by using the celluloid screen. The difficulty in the way of such experiments is the small intensity of the radiations.

Theory of the Action of Charged Points.

The results enumerated above can now be applied to the explanation of the action of a third point or system of points on the spark discharge; but before proceeding to the explanation, it may be well to clear away a preliminary difficulty. Throughout the present paper the action of the third point has been described as a "lowering of the sparking potential." In practice, when an induction coil is the source of energy, this is undoubtedly what occurs. But the term "sparking potential" has a technical meaning which is not implied here. The "sparking potential" across a gap is the potential difference at which a spark will pass, when this potential difference is applied gradually, and is continued for an indefinite time. The effect of "time lag" is thus eliminated, and it is questionable if any external mechanism can cause any lowering of this potential. In the case of an induction coil the peak potential difference is applied for a very short time only, and consequently the "lag" causes an apparent rise in the "sparking potential." The true action of the third point must be described as eliminating this "lag." The preliminary ionization of the gas in the gap takes place more rapidly, and the current rises more quickly to that necessary to produce a spark. "Lowering of the sparking potential" is therefore a vague description of the action of the point. It is merely a convenient expression,

and wherever it occurs in the present paper the above reservations must be kept in mind.

The results described above have led the writer to put forward the following hypothesis :—

1. The lowering of the sparking potential is caused in different ways by different arrangements of points, and the effects of different causes may vary considerably in relative importance as the type of discharge is varied.

2. The two main causes are :—

(*a*) Photo-electric effects due to ultra-violet radiations from small sparks or the air near positive points.

(*b*) Ions produced by the ionization of the gas by radiations which emanate from the air near positively or negatively charged points.

(*a*) The photo-electric radiations are more powerful than the ionizing radiations in any arrangement where there is a positive point at a distance greater than three centimetres from the main gap. At distances greater than three centimetres the ionizing radiations are completely absorbed by the air before they get to the gap, while the photo-electric radiation can, if the main electrodes are of clean zinc, affect the sparking potential when its source is as much as fifteen centimetres away. If the electrodes are dirty or oxidized, however, it is difficult with the same length of gap to obtain an effect at more than three centimetres distance. Similarly the substitution of copper for zinc reduces the range of the effect considerably. These results, along with those described earlier in the paper, show that the photo-electric radiation is of prime importance.

(*b*) The ionizing radiation also affects the sparking potential, but the range of its effect is smaller. Also its action appears to be somewhat complicated. When the distance of a charged point from the spark gap is less than three centimetres, the air in the gap is directly ionized. That this must be the case is shown by the ionization chamber experiments, and it is well known that a spark appears more readily in any gap after previous ionization of the gas in it. But experiments have shown that the radiation can affect the air in the gap when its source is at greater distances. Using the auxiliary gap of fig. 1 *d* and shielding both electrodes from photo-electric radiations, under certain conditions a lowering of the sparking potential is found with the distance

AB to CD equal to four centimetres. The following two experimental facts must therefore be reconciled :

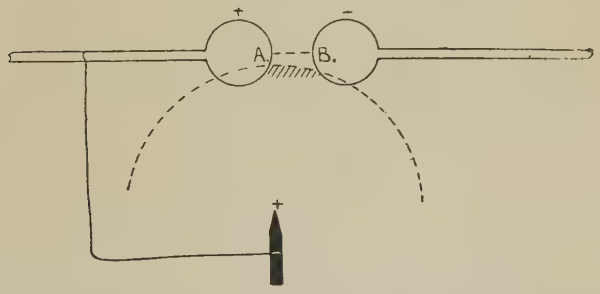
(*a*) The radiation can affect the spark when its source is 4 cm. distant.

(*b*) The range of the radiation is 3 cm. as determined by the tilted electroscope.

The writer has come to the conclusion that the ions produced by the radiation can affect the sparking potential even when they are not in the line of the spark, and suggests the following explanation :—

The ions are produced within the sphere whose central section is indicated by the dotted circle (fig. 8). Ions in the shaded portion of the sphere move under the field of electric force to one or other of the electrodes, the diffusion

Fig. 8.



being negligible, owing to the strength of the field. The energy acquired under the field of force is liberated when the ions strike an electrode and this energy takes the form of pulses of electromagnetic radiation which are probably photo-electric in character. This secondary radiation ultimately penetrates to the line AB and increases the conductivity of the gas there, thus facilitating the passage of the spark. The explanation was suggested by the recent work of Sir J. J. Thomson * on the action of low-velocity ions.

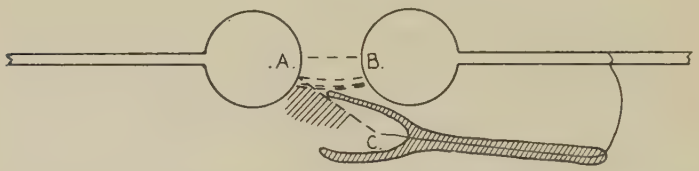
If this hypothesis is correct, it should be possible to effect a lowering of the sparking potential even when the radiating point is "invisible" from the path of the spark, so long as some part of a sphere of radius 3 cm. about the point as centre is "visible" and within about 1 cm. from the spark

* Phil. Mag. vol. ii. p. 675 (1926).

line. To investigate this the following experiment was tried :—

The point C (fig. 9) was sheathed in an open cylinder of clean paraffin-wax and brought up to the gap in the position shown in the diagram. C was "invisible" from any part of the spark, AB, yet a distinct effect was observed. It follows, therefore, that the ionized air in the shaded portion of the diagram was able to cause a lowering of the sparking potential. It is to be noted, however, that a straight line is necessary from C to within less than 1 cm. from AB. Other forms of the experiment just described can be arranged, where, without the use of a shield, C is placed very close to the electrode B. Here, again, an effect can be obtained when no straight line in air exists from C to AB. A striking example of this type of action is observed when the point gap of fig. 1*f* is used. Here the effect will *only* occur if C and D are so close to A and B that no straight line can

Fig. 9.



be drawn to the path of the spark, the radiation emanating from the silent discharges between C and A and between D and B.

Experiments with the Metallic Point connected to a Source of constant potential.

When the metallic point C (fig. 1*b*) was connected to one pole of a Wimshurst machine instead of to one electrode of the main gap, the point was found to have only a slight effect in facilitating the passage of the spark across the main gap AB. The effect was much smaller than the usual three-point effect. It was also noticed that no violet glow could be detected round the point in the dark, and if two such points were connected to the opposite poles of the Wimshurst, no spark could be produced between them. No evidence was found of radiation proceeding from the point under these conditions, although careful tests were made with the ionization chamber. The reason probably is that the point never reached a sufficiently high potential,

the charge leaking from the point very rapidly in the form of an electric wind.

Somewhat similar results were found by Morgan * in the paper already mentioned. That writer also concluded that no radiation was given off by a metallic point connected to the pole of a Wimshurst machine, and that any effect in the main gap in these conditions is due to an ionized stream, proceeding from the point. The experimental results of Morgan are therefore confirmed by the present experiments, but a somewhat different explanation of them is now offered. It was suggested by Morgan that in order that a point should emit an ionizing radiation, its potential should be of an impulsive or transient character. The present writer agrees with this view, but is of the opinion that the transient nature of the potential is only necessary in order that the point should be raised to a sufficiently *high* potential. With a continuous source the potential of the point never reaches a value high enough for the emission of radiation. It does not seem probable that the emission of radiation can depend, as Morgan suggests, on the *time* rate of change of potential of the point, but it does depend, as the present experiments have shown, on the *space* rate of variation of potential near the point.

The Influence of the State of the Cathode Surface on the Effect of the Ionizing Radiation.

A series of experiments was carried out with the object of determining whether the action of the ionizing radiation in lowering the sparking potential of the main gap was affected in any way by the state of the cathode surface. In these experiments the two main electrodes were, of course, entirely shielded from any direct (photo-electric) radiation from the metallic points, the air gap between these being alone in a direct line with the discharge. Otherwise the arrangement of fig. 1 *d* was used. In these circumstances it was found that the state of the surface of the cathode was an important factor in the action. If the cathode surface was dirty or oxidized, the point produced no effect if further than 2·6 cm. from the main gap (AB = 1 cm.). When the cathode surface was cleaned by rubbing with emery paper, the limiting distance of the point was slightly over 3 cm. When the cathode surface was brightly polished, the limiting distance was over 4 cm. Experiments in which different metals were used as main electrodes also led to the same conclusion.

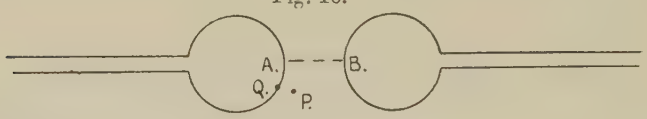
* J. D. Morgan, *loc. cit.*

With a brass cathode the effect was slightly less than with zinc, while with a cathode of copper (whether polished or not) the limiting distance of the point never exceeded 2 cm. These experiments show that, even when no radiation from the metallic point reaches the surface of the cathode directly, the effect of the radiations in lowering the sparking potential depends on the nature of the cathode surface. It was difficult to determine whether the anode surface had any such effect, but, if so, it was certainly very much smaller than the effect of the cathode surface.

Mechanism of the Spark Discharge.

One of the chief facts which emerge as a result of the experiments described in the present paper is that ions produced at some distance from the line in which the main spark passes can in some way facilitate the passage of this spark, and that the intensity of this effect depends upon the nature and state of the cathode surface. These results seem to be in entire agreement with the theory of the spark discharge recently proposed by J. Taylor * and based upon

Fig. 10.



Sir J. J. Thomson's researches on the action of low-velocity positive ions †. An essential feature of this theory is that the positive ions in a low-pressure discharge, when neutralized at the cathode surface, give rise to ultra-violet (Schumann) radiations, and that these radiations, acting as an intermediate cause, produce the liberation of photo-electrons.

In the present experiments a positive ion formed at P (fig. 10), at some distance from the line of spark, AB, is moved under the influence of the intense field to near the point Q of the cathode surface. There it excites ultra-violet radiation which liberates electrons from the metal in the neighbourhood. These electrons travel towards the anode surface, causing ionization by collision with neutral molecules in their paths. The process may repeat itself many times before the disruptive discharge takes place.

* J. Taylor, Phil. Mag. iii. p. 753 (1927); Proc. Roy. Soc. A, 114, p. 73 (1927).

† Phil. Mag. vol. xlviii. p. 1 (1924), and *loc. cit.*

Further evidence in favour of this theory is given by the point discharge itself. As the experiments have shown, electromagnetic radiations of fair intensity emanate from the parts of the discharge path near the points. These radiations are undoubtedly due to the liberation of the kinetic energy of the ions. The differences between the discharge between points and the discharge between spheres are of degree rather than of kind. The field of force in the former case is much more irregular, and the surface density of the electricity is greater in the case of a point than in the case of a sphere, but the discharge mechanism is similar in nature. Consequently, if radiations emanate from the point discharge, it is to be expected that radiations of the same type but of less intensity will be present near the spherical electrodes. That the *visible* radiations from a point discharge can also be obtained from spheres just before sparking takes place was shown many years ago by Walter *. The latter took photographs of sparks on rapidly-moving plates, and found that each spark was preceded by a faintly luminous brush discharge. It is highly probable, therefore, that ultra-violet radiations are present near the spherical electrodes when the potential approximates to that required for a spark to pass.

From these considerations, then, the conclusion may be drawn that the action of the metallic points on sparking potentials is similar to the action of the discharge itself. The behaviour of ions in the line along which the spark passes must be similar to the behaviour of ions outside of this line but within the field of electric force. If this is so, then the current through the gas must depend on the nature of the cathode surface, and some sort of photo-electric action must be assumed to take place. This is the conclusion to which the experiments of Taylor have led : it is not accounted for in Townsend's theory of the spark discharge, in which the positive ions are assumed to produce ions by collision with neutral molecules, but not as a result of their impact on the negative electrode.

That Taylor's hypothesis leads to a formula which gives accurately the current through a gas, when recombination of the ions can be neglected, was shown by Townsend himself †, while in 1923 Dubois ‡ derived a formula which allowed both for ionization by the collision of positive ions and for photo-electric action of the latter at the negative electrode.

* *Wied. Ann.* lxvi. p. 636; lxviii. p. 776.
† 'Electricity in Gases,' pp. 330, 331.
‡ *Ann. de Phys.* t. xx. p. 222 (1923).

Dubois's formula reduces to those given by Townsend when β or γ is made zero. It is

$$N = n_0 \frac{(\alpha - \beta)\, e^{(\alpha-\beta)D}}{\alpha(1+\gamma) - (\alpha\gamma + \beta)\, e^{(\alpha-\beta)D}},$$

where D is the distance between the parallel plate electrodes.

It appears to the writer that the problem of deciding between the "ionization by collision of positive ions" theory and a "photo-electric" theory of sparking potentials resolves itself theoretically into the question whether radiation or ionization by collision occurs first in a discharge. It is known that a collision between an ion and a gas molecule can give rise to a pulse of electromagnetic radiation. It is also known that a collision between an ion and a molecule can cause ionization of the molecule—that is, can cause the molecule to lose an electron. Which of these two phenomena will occur first if the speed of a positive ion is gradually increased? It would appear reasonable to suppose that less energy is required to move an electron from one orbit to another (as when radiation is emitted) than to remove an electron from the molecule entirely (as when ionization occurs); consequently it appears reasonable to conclude that radiation occurs before ionization.

If this view is correct, there can be little doubt that the "photo-electric" theory is true, since sufficient ions can be generated by this means to satisfy the requirements of the sparking current. If, on the other hand, ionization occurs first, then the photo-electric effects will be very subsidiary and of little importance.

It is again urged that the point discharge and the usual spark discharge between spheres or planes differ only in degree. What is found in the one may be expected to be found in the other with the appropriate modifications. But the point discharge gives evidence of radiations from the vicinity of the cathode long before a spark passes. We may therefore expect that the same occurs in a modified way in the spark discharge between spheres.

It may be remarked in passing that one of Townsend's objections to a theory of the discharge in which the positive ions only form others at the cathode, is that the current from a positive point to a negative plane cannot be explained on this hypothesis. In view, however, of the fact that a positive point is the source of electromagnetic ionizing and photo-electric radiations, quite sufficient to account for the current

in these conditions, it would scarcely seem necessary to assume any ionizing action of the positive ions in the point and plane system.

Summary.

1. Experiments are described showing :

i. That electromagnetic radiations emanate from the air in the immediate neighbourhood of charged metallic points from which electric discharges are taking place in air at atmospheric pressure. The intensity of the radiations increases with the intensity of the discharge.

ii. That the radiations produce photo-electric effects and ionization.

iii. That the radiations producing the photo-electric effects emanate only from the neighbourhood of positively charged points.

iv. That the ionizing radiations emanate from the neighbourhood of both positive and negative points.

v. That the photo-electric radiations can penetrate 15 cm. of air at atmospheric pressure.

vi. That the ionizing radiations are absorbed by 3 cm. of air at atmospheric pressure.

2. These results differ from those of Wynn-Williams in regard to the precise locality of the source of the radiations, and in regard to their penetrating powers.

3. A theory is suggested of the action of a charged metallic point in facilitating the passage of a spark between spherical electrodes.

4. This theory differs from that offered by Wynn-Williams in ascribing the greater part of the action to the photo-electric effect.

5. The action of the ionizing radiations in facilitating the passage of the spark is found to depend on the nature and state of the surface of the cathode.

6. The ionizing radiations are found to be capable of facilitating the passage of the spark, even when no straight line can be drawn in air from the metallic point to the line of the spark discharge.

7. It is suggested that the action of the ionizing radiations in such cases is an indirect effect due to the impact of positive ions on the metal of the cathode.

8. The experimental results of Morgan are examined and confirmed, but a somewhat different explanation of them is given.

9. The results of the present experiments are considered

in relation to the theory of the spark discharge recently put forward by J. Taylor, and are found generally to support this hypothesis.

10. Some of Townsend's conclusions with reference to his theory of the spark discharge are considered in the light of the results of the present experiments, and modifications of these conclusions are suggested.

In conclusion, the writer wishes to express his thanks to Professor Taylor Jones for his continued advice and encouragement and for many helpful suggestions. The experimental part of the work was performed in the Research Laboratories of the Natural Philosophy Department of the University of Glasgow.

November 1927.

LIII. *An Extension of Langevin's Theory of Atomic Magnetism to Molecules constituting Electronic Isomers.* *By* Professor S S. Bhatnagar, *D.Sc.* (*London*), *University Professor of Physical Chemistry*, *Punjab University*, *Lahore*, *and* Mr. Chaman Lal Dhawan, *B.Sc.* (*Hons.*) *.

ON modern views regarding the structure of matter it is natural to expect that two molecules containing the same number of electrons and having those electrons grouped in the same way will show a certain similarity of physical properties. This resemblance is closely brought out in the case of nitrogen and carbon monoxide. Caven † has brought out the close likeness in the physical properties of nitrous oxide and carbon dioxide, and has shown that the value of the magnetic susceptibilities of the gases at 40 atmos. at 16° is $0{\cdot}12 \times 10^{-6}$ in both cases.

Both on the Valency Theory of Langmuir and the Atomic Theory of Bohr such should be the case, as these gases constitute identical electronic configuration.

The verification of this view from the standpoint of magnetic data presents special interest. A theory of atomic structure which explains the magnetic properties of atoms and molecules has a lasting future. The periodic curve connecting atomic numbers of elements and their magnetic susceptibilities does not indicate any immediate and strikingly

* Communicated by the Authors.

† 'Structure of Matter,' p. 156 (1924 edition).

simple relations, although a few regularities show up when attention is confined to members of a single family. For example, there seems to be a tendency for the atomic diamagnetic susceptibilities to increase with atomic number. This is clear from the table shown below :—

TABLE I.

	Atomic number.	Atomic magnetic susceptibility.
Cl	17	$19{\cdot}5\times10^{-6}$
Br	35	$32{\cdot}0\times10^{-6}$
I	53	$45{\cdot}7\times10^{-6}$
S	16	$16{\cdot}0\times10^{-6}$
Se	34	$25{\cdot}4\times10^{-6}$
Te	52	$40{\cdot}5\times10^{-6}$
Zn	30	$10{\cdot}2\times10^{-6}$
Cd	48	$20{\cdot}2\times10^{-6}$
Hg	80	$38{\cdot}1\times10^{-6}$

The question of the susceptibilities of the inert-gas configuration has been elegantly treated by Joos*. If we consider the argon atom with 18 electrons, it has the same electronic configuration as the K^+ and Cl^- ions. The magnetic susceptibilities of these substances ought to be identical on the viewpoint of Langmuir. But in passing through the series Cl^-, A, K^+, the ionic (or atomic) susceptibility should decrease as a result of the decrease in size of the electronic orbits owing to the increasing nuclear charge. If Z represents the effective nuclear charge, then for orbits characterized by the same quantum numbers

$$r_1^2 \propto \frac{1}{Z^2}.$$

According to Langevin's theory the diamagnetic susceptibility is given by

$$\chi_{\text{At.}} = -\frac{e^2}{4mc^2}\Sigma_n \bar{r}^2, \quad \ldots\ldots \quad (1)$$

the summation being extended over the n electrons in the

* *Zeit. f. Phys.* xix. p. 347 (1923); *ibid.* xxxii. p. 835 (1925).

atom, and $\bar{r}^2$ being the mean square of the radius of the projected orbit in a plane perpendicular to the field.

For K^+ and Cl^- therefore as a sufficiently close approximation from (1) one gets the relation

$$\chi_{K^+} : \chi_{Cl^-} = \frac{1}{(19)^2} : \frac{1}{(17)^2}.$$

Joos has thus got the values of K, Cl, and A as follows :—

K	15·5
A	17·5
Cl	19·5

The value of argon is in excellent agreement with the experimental values of Hector and Wills *. The values of K and Cl are also in good agreement with recognized experimental values.

Following the lead of Joos, we have tried to explore the possibility of finding a simple relationship between the values of molecular magnetic susceptibilities of electronic isomers and the isomorphous substances belonging to the same family and the radii of these molecules.

The radii of these molecules may be calculated from the values of the diameters of the atoms constituting a molecule. The question, however, arises as to what is meant by the diameter of an atom. From the point of view of the Kinetic Theory the diameter, or rather the sum of the radii of the two atoms would be the minimum distance between the centres of two colliding atoms. The closeness with which two atoms subject to electrical repulsions would approach would obviously depend upon their relative speeds, so that the dimensions of atoms calculated from the mean velocity of the molecules of a gas would apparently give the mean of varying diameters. The second view of regarding the diameter of the atom is to identify it with the diameter of the orbit of the outermost electron.

A third method of regarding the atomic diameter is used by W. L. Bragg †. In our calculations for the radii of the molecules use has been made of the values of the atomic diameters of elements as obtained by W. L. Bragg. For example, in the case of the isomorphous series $BaCO_3$, $SrCO_3$, $MgCO_3$, $CaCO_3$ the radii of the constituent atoms are as follows :—

* Phys. Rev. xxiii. p. 209 (1924).
† Phil. Mag. xl. p. 169 (1920).

TABLE II.

Names.	Atomic radii of metallic particles.	Atomic radius from O.	Atomic radii for 3 atoms of oxygen.
$BaCO_3$	2·10	0·77	3×0·65
$SrCO_3$	1·95	0·77	3×0·65
$CaCO_3$	1·7	0·77	3×0·65
$MgCO_3$	1·425	0·77	3×0·65

The radii of the molecules have not been obtained by adding up, as this would hardly represent the exact state of affairs in molecule-building. A more correct way will be to calculate the radius from the volume of the new sphere formed by the closest packing of the atoms constituting the molecules by employing the following equation :

$$\tfrac{4}{3}\pi r_n^3 = \{\tfrac{4}{3}\pi r_1^3 + \tfrac{4}{3}\pi r_2^3 + \ldots\},$$

from which

$$\bar{r}_n = \{r_1^3 + r_2^3 + \ldots\}^{\frac{1}{3}}.$$

The radii of the molecules discussed in this communication calculated on the above view are shown in the table below :—

TABLE III.

Substance.	$\bar{r}_n$ calculated.
$BaCO_3$	2·193
$SrCO_3$	2·056
$CaCO_3$	1·836
$MgCO_3$	1·620
KNO_3	2·156
$NaNO_3$	1·884
$NaClO_3$	2·41
$KHSO_3$	2·58
$SrSO_1$	2·086
$KClO_4$	2·254
*NaCl	2·825
*CaO	2·35
*AgCl	2·825
*BaO	2·750
$CaSO_4$	1·922
K_2CO_3	2·675
*NaF	2·45
*MgO	2·075

* In the case of compounds containing only two atoms, the radii have been calculated by simple addition. This is as it should be.

TABLE III. (*continued*).

Substance.	r^n calculated.
Isobutylaldehyde.....	1·305
Methylethylketone	1·305
Phenyl acetate	1·620
Methyl benzoate	1·620
Ethylaniline	1·601
Dimethylaniline	1·601
TeH_2O_3	1·471
$ZnSO_4$	1·051
Glycerine	1·323
Aniline	1·461

In Table IV. we have assembled the values of magnetic susceptibilities of some substances which are isomorphous and whose elements constituting the molecules have also close family resemblances with each other. These values are shown against their radii, calculated on the equation of closest packing :—

TABLE IV.

Names.	$\chi_m \times 10^{-6}$. Experimental.	Radii of the molecules calculated on the equation of closest packing.
$BaCO_3$	43·42	2·193
$SrCO_3$	25·25	2·056
$CaCO_3$	14·01	1·836
$MgCO_3$	6·999	1·620

An examination of this table shows at once that there is a decrease in the magnetic susceptibility of the compound as the radius of the molecule is decreased, a conclusion which is in line with the views of Joos regarding the variation of the value of magnetic susceptibility with the change in the value of $\bar{r}^2$ in the case of atoms constituting electronic isomers (*loc. cit.*).

Now, according to Langevin's theory

$$\chi_{At.} = -\frac{e^2}{4mc^2}\Sigma_n \bar{r}^2.$$

Multiplying this by the Avogadro number, we get

$$\chi_{At.} = -2{\cdot}85 \times 10^{10} \Sigma \bar{r}^2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and for a molecule constituting an electronic isomer or an isomorphous body equation (2) may be written as

$$\chi_m = -2{\cdot}85 \times 10^{10} \Sigma (K\bar{r}_1)^2, \quad . \quad . \quad . \quad . \quad (3)$$

where $\bar{r}_1$ represents the value of the radius of the molecule calculated as described before and K is an arbitrary constant, but which in a series of isomers is found to exhibit variations depending upon the summation of the atomic numbers extending over all the atoms constituting the molecule. Its significance has been discussed later on in this paper.

We shall try to verify the equation adopted, *i. e.* $K_m = -2{\cdot}85 \times 10^{10} \Sigma (Kr_1)^2$, by calculating the value of K_m for electronic isomers and isomorphous series (both organic and inorganic).

The results obtained by calculation from equation (3) are tabulated against the experimental values (most of which are taken from the Physico-Chemical Tables of Landolt and Börnstein). Some values which were not known have been determined experimentally in our laboratory by Mr. S. L. Bhatia, M. Sc., and are communicated for publication in a paper by him.

TABLE V.

Case of Isomorphous substances belonging to the same family.

Names.	$\chi_m \times 10^{-6}$. Experimental.	$\chi_m \times 10^{-6}$. Calculated from equation (3).
$BaCO_3$	−43·42	−52·46
$SrCO_3$	−25·25	−29·18
$CaCO_3$	−14·01	−13·28
$MgCO_3$	− 6·999	− 7·17
KNO_3	−33·66	−33·66
$NaNO_3$	−26·35	−20·91

TABLE VI.

Case of Electronic Isomers (Inorganic).

Atomic number.	Names.	$\chi_m \times 10^{-6}$. Experimental.	$\chi_m \times 10^{-6}$. Calculated on equation (3).
28	NaCl.....	−23·98	−22·94
28	CaO	−15·12	−15·74
64	BaO	−18·40	−21·55
64	AgCl.....	−40·13	−31·99
20	NaF	−11·76	−10·95
20	MgO	− 6·73	− 7·83
68	K_2CO_3	−76·02	−81·57
68	$CaSO_4$	−51·73	−43·0
78	TeH_2O_3.....	−33·72	−33·68
78	$ZnSO_4$	−43·58	−42·44

TABLE VII.

Case of Electronic Isomers (Organic).

Atomic number.	Names.	$\chi_m \times 10^{-6}$. Experimental.	$\chi_m \times 10^{-6}$. Calculated on equation (3).
40	$CH_3 . CH_2 . CH_2CHO$ Isobutylaldehyde	−47·45	−47·56
40	$CH_3 \diagdown CO$ $C_2H_5 \diagup$ Methylethylketone	−47·74	−47·56
72	$CH_3COOC_6H_5$ Methyl benzoate	−83·23	−82·90
72	$C_6H_5COOCH_3$ Phenyl acetate	−82·69	−82·90
66	$C_6H_5NHC_2H_5$ Ethylaniline	−89·30	−89·4
66	$C_6H_5N(CH_3)_2$ Dimethylaniline	−89·66	−89·4
50	$OH . CH_2 . CHOH . CH_2OH$ Glycerine	−56·12	−53·31
50	$C_6H_5NH_2$ Aniline	−65·1	−65·1

It is to be noted that the agreement between the experimental and the calculated values of χ_m in the case of electronic isomers is excellent. In the case of isomorphous series (Table V.) the agreement is fair.

Significance of K *employed in Equation* (3).

K is an arbitrary constant characteristic of a particular group of electronic isomers. The values of χ have been assembled in Table VIII. In this table the ratios of K for a set of substances have been compared with the ratios of the summation of atomic numbers constituting these molecules. A very characteristic relationship is at once noticeable.

TABLE VIII.

Substance.	Summation of atomic numbers of elements constituting the compound.	Value of K.	Ratio of the summation of atomic numbers.	Ratio of K.
I.				
$BaCO_3$	86	1·96	86/42=2·0	1·96 /0·98 =2·0
$SrCO_3$	68	1·56	68/42=1·6	1·56 /0·98 =1·6
$CaCO_3$	50	1·176	50/42=1·19	1·176/0·98 =1·19
$MgCO_3$	42	0·98	42/42=1·0	0·98 /0·98 =1·0
II.				
KNO_3	50	1·7	50/42=1·19	1·7 /1·43 =1·19
$NaNO_3$	42	1·43	42/42=1·0	1·43/1·43 =1·0
III.				
$NaClO_3$	52	1·55	52/52=1·0	1·55 /1·55 =1·0
$KHSO_3$	60	1·788	60/52=1·15	1·788/1·55 =1·15
IV.				
NaCl	28	1·0	28/28=1·0	1·0/1·0 =1·0
CaO	28	1·0	28/28=1·0	1·0/1·0 =1·0
V.				
AgCl	64	1·184	64/64=1·0	1·184/1·184=1·0
BaO	64	1·184	64/64=1·0	1·184/1·184=1·0
VI.				
$CaSO_4$	68	2·0	68/68=1·0	2/2 =1·0
K_2CO_3	68	2·0	68/68=1·0	2/2 =1·0

TABLE VIII. (*continued*).

Substance.	Summation of atomic numbers of elements constituting the compound.	Value of K.	Ratio of the summation of atomic numbers.	Ratio of K.
VII.				
NaF.....	20	0·8	20/20=1·0	0·8/0·8 =1·0
MgO	20	0·8	20/20=1·0	0·8/0·8 =1·0
VIII.				
Isobutaldehyde ...	40	3·131	40/40=1·0	3·131/3·131=1·0
Methylethylketone	40	3·131	40/40=1·0	3·131/3·131=1·0
IX.				
Phenyl acetate ...	72	3·311	72/72=1·0	3·311/3·311=1·0
Methyl benzoate...	72	3·311	72/72=1·0	3·311/3·311=1·0
X.				
Ethylaniline	66	3·497	66/66=1·0	3·497/3·497=1·0
Dimethylaniline .	66	3·497	66/66=1·0	3·497/3·497=1·0
XI.				
TeH_2O_3	78	2·337	78/78=1·0	2·337/2·337=1·0
$ZnSO_4$.....	78	2·337	78/78=1·0	2·337/2·337=1·0
XII.				
Aniline	50	3·271	50/50=1·0	3·271/3·271=1·0
Glycerine	50	3·271	50/50=1·0	3·271/3·271=1·0

It is seen that the values of the constant K in a series are proportional to the atomic numbers. In the case of isomorphous series (Nos. I. and II. in the table) the value of K decreases as the summation of atomic number decreases. In the case of electronic isomers the values of K are identical. A very characteristic feature of K is that it is roughly proportional to the number of atoms contained in the molecules. For example, in the case of molecules containing two atoms K has an approximate value of 1 (0·8 to 1·184). For molecules containing four to five the mean value of K is about 1·5 to 1·6 (ranging between 1·43 to 1·96). For molecules containing six atoms it is approximately 2, and rises continuously as the atoms in the molecules are increased. Thus, in the case of iso-butaldehyde and methylethylketone, where the number of atoms is 13,

the value of K is 3·131. In the case of phenyl acetate and methyl benzoate, with 18 atoms, the value of K is 3·311, and for ethylaniline and dimethylaniline, with 20 atoms, the value of K is 3·497. These regularities about the constant suggest that equation (3) may be of fundamental physical significance.

Further work on the magnetic susceptibilities of electronic isomers is in progress.

The authors take this opportunity of thanking Messrs. K. N. Mathur and S. L. Bhatia.

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LIV. *Supplementary Note on the Parallel-plate Condenser in Two Dimensions. By* Doris Mona Hirst, *M.A., and* W. B. Morton, *M.A., Queen's University, Belfast* *.

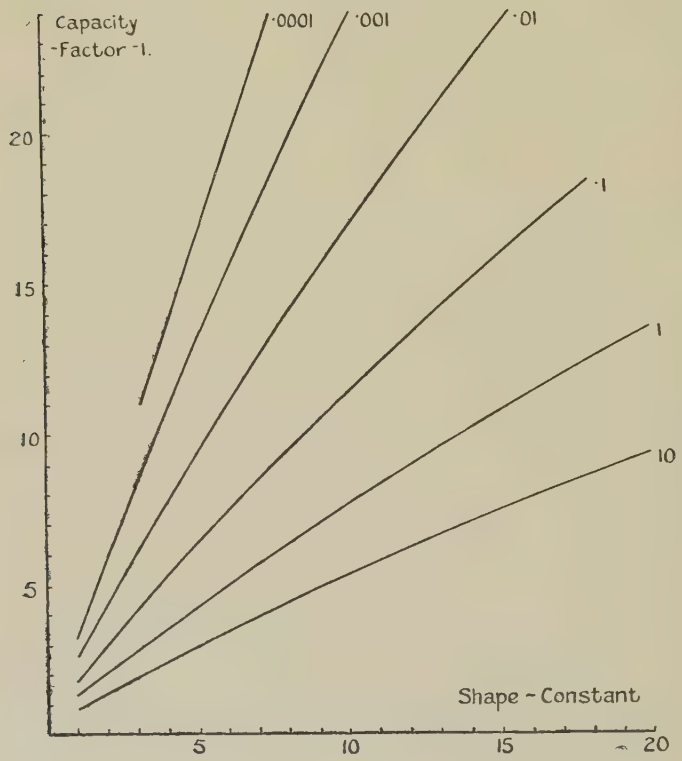
IN a note which appeared in this Magazine for October 1926† there was given, along with other results, a graph connecting the "capacity-factor" and the "shape-constant" of a condenser formed by long parallel strips (*loc. cit.* fig. 8). By capacity-factor is meant the ratio of the capacity, per unit length, to the value which would be derived from the elementary formula, on the supposition that the lines of force between the plates are everywhere straight. The shape-constant is the ratio of the distance between the plates to the breadth of either plate. These magnitudes are functions of the modulus of the elliptic functions used to express the solution, and the plates come close together as the modulus approaches unity. Unfortunately, the logarithmic manner in which K becomes infinite at the limit has the consequence that the shape-factor is comparatively large even when the modular angle is quite near to 90° ; its value is ·459 for 89°, so that the capacity, when the planes are closer than this, cannot be calculated by use of Legendre's tables without interpolation. Thus the most interesting part of the graph, corresponding to planes which are close together, was only obtained on a small scale as a prolongation of the curve towards the origin.

* Communicated by the Authors.

† W. B. Morton, "On the Parallel-plate Condenser and other Two-dimensional Fields Specified by Elliptic Functions," Phil. Mag. ii. p. 827 (1926).

The object of the present note is to extend the calculated range in this direction. The numerical values were computed by expanding the functions in powers of 1/K. The results are shown on the accompanying diagram. In order to give adequate representation of the entire range of values the graph has been broken into a number of pieces on different

Fig. 1.



scales. The magnitude marked on each curve is the value to be assigned to the unit of the scales marked along the axes. It will be noticed that even at the smallest values the curve still makes a considerable angle with the vertical axis, although it ultimately touches this axis at the origin.

The following values of the capacity-factor, for selected shapes of condenser, were calculated by interpolation, and are quoted to give an idea of the magnitude of the correction.

Shape-constant 1,		Capacity-factor	2·118
„	·1,	„	1·168
„	·01,	„	1·024

The smallest values calculated were ·000315 and 1·00109, shape-constant and capacity-factor corresponding to K = 5000.

This work was done without knowledge of any previous investigation, except that of Sir Joseph Thomson, mentioned in 'Recent Researches' and quoted in the former note. We owe to Dr. Bromwich a reference to two papers on the same subject—one by J. H. Michell *, published in 1893, the year in which 'Recent Researches' appeared, and the other by Dr. Bromwich himself † in 1902. In the former paper expansions are given equivalent to those which we have used, but in terms of log $4/k'$ and k' instead of 1/K. In Dr. Bromwich's work the problem is solved directly by Schwarz's method, and Weierstrass's functions are used.

LV. *On the Acoustics of Strings struck by a Hard Hammer.* *By* K. C. Kar, *D.Sc.*, R. Ganguli, *M.Sc.*, *and* S. C. Laha, *M.Sc.*‡

Introduction.

THE theoretical treatment of the problem of struck strings has proceeded on two different lines. To the first class of theories belong those put forward by Helmholtz §, Delemer ‖, and Lamb ¶, each of which is based on some assumed law of pressure between the hammer and the string during the time of contact. The second method of attacking the problem is due to Kaufmann **, who gives a rigorous functional solution—provided the duration of contact (t) is less than but comparable with the free period (θ) of the string $\left(\text{i. e. } \frac{t}{\theta} < \frac{l-a}{l}\right)$—of the case of a massive particle striking (1) a string of infinite length, (2) a string of finite length at its centre or very near the end. In the case when the

* J. H. Michell, Quarterly Journal of Mathematics, xxiii. p. 72 (1893).
† T. J. I'a. Bromwich, Messenger of Mathematics, xxxi. p. 184 (1902).
‡ Communicated by the Authors.
§ Helmholtz, 'Sensations of Tone.'
‖ Delemer, *Ann. Soc. sci. de Bruxelles*, xxx. pts. 3–4, pp. 299-310 (1905–6).
¶ Lamb, 'Dynamical Theory of Sound,' p. 74.
** Kaufmann, *Wied. Ann.* liv. pp. 675–712 (1895).

hammer strikes the string near its end, Kaufmann has, however, assumed that the portion of the string between the hammer and the nearer end vibrates as a rigid rod. This assumption of Kaufmann has been done away with by P. Das *, who, however, makes the further assumption that the hammer gives discontinuous impulses to the string during the time of contact, the time between two successive impulses being the time taken by a wave to start from the hammer and to come back to it after reflexion from the nearer end. With the above assumption Das has extended Kaufmann's theory by proceeding on a line similar to that of Love † for the longitudinal vibration of a string struck at the end.

The experimental work in this direction has been done by Kaufmann ‡ himself and also by Hipkins §, who find no agreement with the Helmholtz-Delemer-Lamb theories. The recent experiments of George ‖ and R. N. Ghose ¶ generally support Kaufmann's theory. Recently Datta ** has also got results which go to support Das's theory. Systematic data on struck strings appear to be still wanting In conclusion, we may make a note of Hayashi's †† experiment, where vain attempts have been made to reach the conditions demanded by Helmholtz's theory.

The above is a summary, made up to date, of George's introduction to his paper appearing in Phil. Mag. xlvii. p. 591 (1924).

In the present paper, attempts have been made (1) to study the amplitudes of the different harmonics for different striking-points when $\frac{t}{\theta} >$ or $< \frac{l-a}{l}$, t being the duration of contact, θ the free period of vibration; (2) to subject Das's theory to an experimental test; (3) to determine the impulses given by the hammer to the string at different

* P. Das, Proc. Ind. Assoc. vii. pts. 1 & 2, pp. 13–20 (1921).

† Love, 'Theory of Elasticity,' pp. 411, art. 281 (2nd ed.).

‡ Kaufmann, *l. c.*

§ Hipkins, Proc. Roy. Soc. xxxvii. pp. 37–39, and xxxviii. pp. 83 (1884).

‖ George, Phil. Mag. xlviii. pp. 34 & 48 (1924), l. pp. 91–99 (1924); Proc. Roy. Soc. cviii. pp. 284–295 (1925). George & Beckett, Proc. Roy. Soc. A, cxiv. (1927).

¶ R. N. Ghose, Phil. Mag. xlvii. p. 1125 (1924); Proc. Ind. Assoc. ix. pp. 111, 194 (1925); Phys. Rev. xxiv. p. 456 (1924), xxviii. p. 1315 (1926).

** S. K. Datta, Proc. Ind. Assoc. viii. pt. ii. (1923).

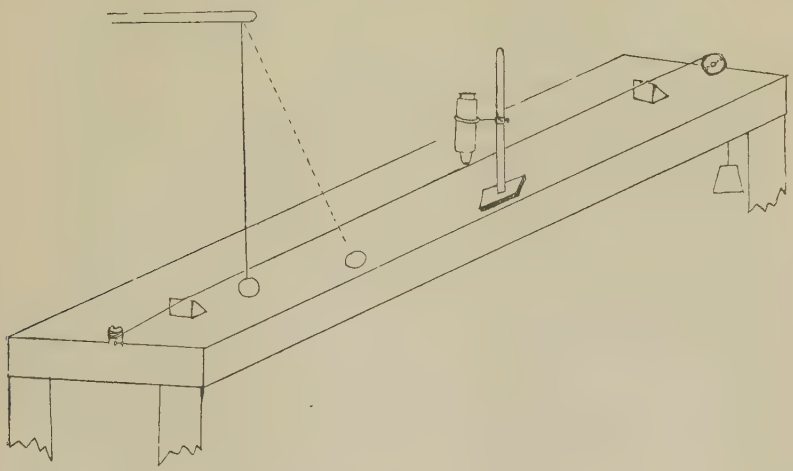
†† Hayashi, Kyoto Coll. Sci. Mem. vi. pp. 165–169 (1923).

points ; and (4) to study the effects of the material and the area of contact of the hammer on the changes of amplitudes of different harmonics.

Experiment.

The experimental wire was horizontally stretched over two bridges fixed on the table. The wire was fixed at one end, and the other end, passing over a rigidly-fixed pulley, carried a heavy weight. The striking-hammer consisted of a metal ball suspended freely by means of a fine thread, thus constituting a simple pendulum. When at rest the bob just touched the wire, and the centre of the bob and the wire lay in the same horizontal plane. Thus struck by the bob-

Fig. 1.



hammer the stretched wire began to vibrate in a horizontal plane. A reading microscope of Becker & Co. of magnifying power 40 was focussed on the wire from above (*vide* fig. 1). We may note, in conclusion, that by the above arrangement we can vary the velocity of impact at will.

In order to measure the amplitude of the fundamental, the microscope was focussed on the middle of the wire, which was illuminated by sunlight from below. The bob being taken aside was released and allowed to strike the wire only once, and the amplitude of vibration was determined by the micrometer scale with the eyepiece, one smallest micro

division being equal to ·027 mm. Again, to get the amplitude of the octave, observations were taken with the microscope at $l/4$, while the wire was damped at the middle immediately after the impact so as to stop the fundamental. Similarly, for the other harmonics, readings were taken with the microscope at an antinode, the corresponding node being damped immediately after impact. The different amplitudes as observed by the microscope were then corrected for the amplitudes of other harmonics for which the point of observation is an antinode. For instance, from the observed amplitude of the fundamental was subtracted the amplitudes of the 3rd, 5th, and so on, and similarly for others.

The results of our investigations are given in three sections.

In section A, Tables I. and III. give the corrected amplitudes of the first six harmonics for different striking-points along wires of steel and eureka. In Tables II. and IV. are given the amplitudes of the fundamental, and the displacements of the centre of the string at the instant of impact when the hammer strikes the wire at different points with different velocities. In section B, Das's equation has been put to an experimental test. The theoretical and the experimental values of different harmonics are compared in Table V. In section C, Table VI. gives the impulses imparted to the string by the hammer striking with different velocities at different points on the string. And in Table VII. are given the changes of amplitudes of the first three harmonics with changes of the area of contact and the material of the hammer.

The values given in different tables are generally means of about ten observations.

Results.

Section A.

Steel wire :—

Mean diameter of the wire	·38 mm.
Mass per unit length	·00892 gm.
Length of the vibrating wire ...	290 cm.
Tension in the wire	3·5 kg.

Striking-bob of iron :—

Mean diameter.....	3·2 cm.
Mass of the bob	140·7 gm.

TABLE I.

Initial velocity of impact—60·11 cm./sec., $\frac{t}{\theta} > \frac{l-a}{l}$.

a—distance of striking-point from nearer end.

a (cm.)	Amplitude of Harmonics (in mm.)*.					
	1st.	2nd.	3rd.	4th.	5th.	6th.
20	2·8047	·3370	·0940	·0405	·0573	·0270
29	2·1602	·2835	·1458	·0810	·0240	·0405
32	2·6935	·4320	·1620	·1215	·0945	·0112
40	1·1131	·4590	·1215	·1080	·0054	·0270
50	2·4191	·1080	·1485	·0810	·0324	·0540
60	2·0312	·3100	·1134	·0675	·0054	·0124
70	1·4056	·5940	·1485	·0405	·0459	·0270
80	2·8447	·8050	·0810	·1134	·0243	·0405
90	1·2299	·5030	·0945	·0540	·0756	·0200
100	2·0218	·2160	·1215	·0540	·0567	·0540
110	1·7992	·4750	·0945	·0648	·0513	·0540
120	1·6448	·4620	·1512	·0810	·0540	·0130
130	1·7380	·5070	·1215	·0567	·0405	·0540
140	1·6353	·4050	·1512	·1080	·0134	—

* Amplitudes of harmonics beyond the 6th were too small to be measured by the microscope at our disposal.

Now, for a string struck at mid-point the maximum value of the displacement, according to Kaufmann's theory †, is given by the equation:

$$y = \frac{v_0 \theta m}{4\mathrm{M}} \left\{ 2e^{-\frac{1}{2}e^{-\frac{2\mathrm{M}}{m}}} \right\}, \quad \ldots \quad (1)$$

where y=the max. displ., v_0=vel. of the hammer before impact, θ=the free period of the string, m=the mass of the hammer, and M=the mass of the string. Substituting the experimental values of v_0, θ, m, and M for the eureka wire and brass hammer, we find y=1·11 cm., whereas from Table IV. y=1·01 cm. Such a close agreement between

† Kaufmann, *l. c.* See also George, Phil. Mag. xlvii. p. 591 (1924).

TABLE II.

v—velocity of the hammer before impact.
y—displacement at mid-point.
F—amplitude of the fundamental.

a (cm.).	v cm./sec.	y (cm.).	F (cm.).	y/v $\times 10^{-3}$.	F/v $\times 10^{-3}$.
10	44·86	·65	...	14·4	
	89·72	1·24	...	13·8	
	112·10	1·51	...	13·4	
20	44·86	·88	·280	19·0	6·24
	89·72	1·59	·600	17·7	6·68
	112·10	1·91	·784	17·0	7·00
40	44·86	1·12	·111	24·9	2·48
	89·72	2·10	·184	23·4	2·06
	112·10	2·53	·304	22·6	2·71
70	44·86	1·49	...	33·2	
	89·72	2·82	...	31·4	
	112·10	3·48	...	31·0	
90	44·86	1·68	...	37·4	
	89·72	3·15	...	35·1	
	112·10	4·00	...	35·5	
110	44·86	1·95	...	43·4	
	89·72	3·50	...	39·0	
	112·10	4·40	...	39·2	
130	44·86	2·10	...	46·8	
	89·72	4·10	...	45·7	
	112·10	5·10	...	45·5	

the experimental and the theoretical values is a good confirmation of Kaufmann's theory. For the steel wire the experimental value of y (=2·5 cm. from Table II. for v=44·86 cm./sec.) is much less than the theoretical value 22·3 cm., as it should be due to the fact that in this case * $\frac{t}{\theta} > 1$. It appears from Table II. that the displacement of the centre of the wire at the instant of impact, as also the amplitude of the fundamental, are approximately proportional to the velocity of impact of the hammer, the constant of proportionality depending on the striking-point.

* t is roughly found to be of the order ·1 sec.

Eureka wire:—

Mass per unit length of the wire ... ·0569 gm.
Length of the wire ..... 290 cm.
Tension in the wire ..... 11 kg.

Striking-bob of brass:—

Mass of the bob ..... 26·5 gm.
Mean diameter of the bob ..... 2·38 cm.
Velocity of the bob before impact . 89·72 cm./sec.

TABLE III.

a (cm.).	Amplitude of Harmonics (mm.).					
	1st.	2nd.	3rd.	4th.	5th.	6th.
10	3·2035	·4050	·6210	·0972	·1755	·0540
20	4·9030	·2700	·2160	·2700	·0810	·0810
29	5·4250	·3510	·4860	·0810	·1890	·0540
40	5·9438	·0675	·4320	·2160	·1242	·0101
50	5·8380	·0540	·1620	·0756	·0110	·0270
60	4·4600	·2025	·4320	·1485	·1080	·0945
70	3·4060	·2700	·5130	·2025	·0810	·1620
80	2·3992	·2800	·4050	·3780	·1458	·0972
90	1·8520	·2970	·4050	·1080	·2430	·0810
100	3·5545	·4860	·3240	·2700	·1215	·0810
110	3·3115	·3240	·4860	·0945	·2025	·0270
120	3·9680	·3240	·2700	·3510	·1620	·0120
130	2·8925	·2970	·5400	·0945	·0675	·0540
140	2·4600	·2430	·4050	·2700	·1350	·0810

TABLE IV.

a (cm.).	y (mm.).	Uncorrected Amplitude of the Fundamental (mm.).
10	4·00	4·00
20	5·20	5·20
29	6·10	6·10
40	6·50	6·50
50	7·00	6·01
60	7·50	5·00
70	8·10	4·00
80	8·52	2·94
90	9·00	2·50
100–140	10·10	—

On comparing the displacements and the uncorrected amplitudes of the fundamental*, *i. e.* the amplitude of vibration of the string as given in Table IV., we find that the two are equal up to about L/7, when the amplitude of the fundamental is maximum for the first time. After L/7 the displacement goes on increasing while the fundamental decreases. Again, with steel wire and iron hammer we find from Table I. that the amplitude of vibration of the wire never exceeds 3 mm. By extrapolation we find that the displacement of mid-point is 3 mm. when the hammer strikes at about L/77. Thus the fundamental should be maximum when the striking-point is at about L/77.

Again, according to George †, for $m/M=1$ the fundamental is maximum at L/7, while for $m/M=9{\cdot}625$ the maximum is at L/30. In our case, for $m/M=1{\cdot}606$ the maximum is at L/7·2. Thus on extrapolating we find that for $m/M=54{\cdot}39$ the maximum is at about L/80. And this agrees fairly well with the value found otherwise. Thus one is led to think that the displacement of the centre and the amplitude of vibration of the wire first begin to differ from the point where the fundamental is maximum for the first time. It may also be noted, in conclusion, that the maxima and the minima of the fundamental and other harmonics become fewer and less pronounced as the relative mass of the hammer (m/M) is reduced.

Section B.

We have already pointed out in our introduction that P. Das ‡ has started with the assumption that the hammer gives discontinuous impulses at $t=0, \frac{2a}{c}, \frac{4a}{c}, \ldots$; *i. e.*, the times at which the waves starting from the hammer come back to it after successive reflexions from the nearer end. Now, according to Das, the pressures in the successive epochs are given by the equations :

$$F_1 = 2\rho v_0 c e^{-kct}, \quad \ldots \quad (2\,a)$$

$$F_2 = 2\rho v_0 c \left[e^{-kct} + e^{-k(ct-2a)}\{1-k(ct-2a)\}\right], \quad \ldots \quad (2\,b)$$

$$F_3 = 2\rho v_0 c \left[e^{-kct} + e^{-k(ct-2a)}\{1-k(ct-2a)\} + e^{-k(ct-4a)}\{1-2k(ct-4a)+\frac{k^2}{2!}(ct-4a)^2\}\right], \quad (2\,c)$$

and so on,

* Obtained by adding ampls. of 1st, 3rd, 5th harmonics.

† George, Phil. Mag. l. p. 495 (1924).

‡ P. Das, *l. c.*

where ρ = mass per unit length of the string, m = mass of the hammer, $k = \frac{2\rho}{m}$, c = velocity of propagation of transverse waves on the string, v_0 = initial velocity of the hammer, a = distance of the striking-point from the nearer end, and t = the variable time.

Thus at time $t=0$ the pressure suddenly increases to $2\rho v_0 c$, and then continuously decreases till the reflected pulse arrives at the hammer at time $t = \frac{2a}{c}$. During this time, which is the first epoch, the pressure is given by eq. (2 *a*). At $t = \frac{2a}{c}$ the pressure suddenly increases by $2\rho v_0 c$, and again goes on falling according to equation (2 *b*). Thus at the beginning of every epoch the pressure increases by an equal jump, $2\rho v_0 c$, and then falls off continuously till after a number of epochs the impact ceases. Having got the pressure-time curve between $t=0$ and $t=\mathrm{T}$, where T is the duration of contact, we proceed to calculate the values of the amplitudes of different harmonics with the help of the well-known equation (notations being same as in eq. 2) :

$$\phi_s = \frac{2}{s\pi c\rho} \sin \frac{s\pi a}{l} \int_0^{\mathrm{T}} \mathrm{F} \sin n_s(t-t')\, dt', \quad . \quad . \quad (3)$$

where T = the duration of contact, l = the length of the string, and $n_s = \frac{s\pi c}{l}$. The above equation can also be written as

$$\phi_s = \frac{2}{s\pi c\rho} \sin \frac{s\pi a}{l} \left[\sin n_s t \int_0^{\mathrm{T}} \mathrm{F} \cos n_s t'\, dt' - \cos n_s t \int_0^{\mathrm{T}} \mathrm{F} \sin n_s t'\, dt' \right]. \quad (4)$$

Thus for the numerical computation of eq. (4) we multiply each ordinate of the pressure-time curve by $\cos n_s t'$ and $\sin n_s t'$ respectively, and obtain two new curves for each harmonic. The areas of these curves between $t=0$ and $t=\mathrm{T}$ give the values of the two integrals in eq. (4). The areas were measured with a planimeter, and the amplitudes of different harmonics were obtained by putting $s=1$, 2, 3, etc. The calculated and the experimental values of the amplitudes of the first six harmonics for the eureka

wire and brass hammer under the experimental conditions prevailing are given as follows :—

Table V.

Harmonics.	Striking-point L/10.		Striking-point L/7·2.	
	Observed.	Calculated.	Observed.	Calculated.
	mm.	mm.	mm.	mm.
First	5·4250	6·8130	5·9438	5·4710
Second	·3510	1·5750	·0675	·6304
Third	·4860	2·6140	·4320	·1808
Fourth	·0810	2·3900	·2160	·1709
Fifth	·1890	·4461	·1240	·5500
Sixth	·0540	·0909	·0101	·5676

Thus there is no agreement between the theoretical and the observed values, even if some allowance be made for the dissipation of energy in the system and for the fact that some time must elapse, however small, between the striking of the hammer and the measurement by the microscope. It may also be noted that from Das's theory the total impulses given by a brass hammer to the eureka wire (used in our exp.) at L/10 and L/7·2 are equal to 3026 and 3841 gm. wt., whereas the corresponding observed values are 4425 and 4376 gm. wt Thus Das's theory goes against experimental evidence.

Before concluding this section we should like to make a few remarks on Mr. Datta's work under Prof. Raman's guidance, already referred to in the introduction. Mr. Datta seems to have made a serious error in taking $\int^{\cdot} F \frac{\cos}{\sin} n_s t' \, dt'$ "between the limits $t=0$ and the time where the curve cuts the axis of time." It is quite obvious*, however, that the other limit will be T, the time of contact between the hammer and the string. Further, he seems to have ignored the fact that n_s within the above integral is different for different harmonics. These have, we think, vitiated his calculations

* Rayleigh, 'Theory of Sound,' vol. i. *l. c.*

throughout. Moreover, he has refrained from giving sufficient data (*e.g.* tension or frequency of the wire), thus making it impossible to repeat his experiment or to check his calculations. At any rate, we fail to see how he could get such a close agreement (sometimes up to 4th place of decimal) between his experimental and theoretical values.

Section C.

TABLE VI.

With steel wire and iron ball described in Sec. A.

a (cm.).	Velocity of hammer before impact, v_i.	Velocity of hammer after impact, v_a.	$m(v_i - v_a)$.	Velocity of hammer before impact. v_i'.	Velocity of hammer after impact, v_a'.	$m(v_i' - v_a')$.
	cm./sec.	cm./sec.		cm./sec.	cm./sec.	
20	44·86	42·83	12340	60·11	55·04	16200
29	,,	44·18	12530	,,	57·19	16500
40	,,	43·86	12480	,,	56·25	16370
50	,,	43·77	12470	,,	55·84	16310
60	,,	43·41	12420	,,	55·11	16350
70	,,	43·37	12410	,,	55·66	16290
80	,,	44·22	12540	,,	56·20	16360
90	,,	43·95	12510	,,	56·87	16450
100	,,	44·40	12560	,,	56·79	16440
110	,,	43·60	12450	,,	55·89	16300
120	,,	42·97	12360	,,	56·34	16390
130	,,	43·46	12430	,,	54·95	16190

Table VI. shows that the impulses imparted to the string pass through a number of maxima and minima as the striking-point is shifted towards the centre from one end. It is of interest to note that in the case of steel wire and iron hammer under consideration the impulse is maximum at about L/10 and L/4. It appears from Table VII. that the nature of the metal of the hammer plays an important part in determining the amplitudes of the harmonics. Further, as the area of contact is increased by increasing the size of the brass hammer, the fundamental is considerably weakened.

Table VII.

Steel wire under experimental conditions given in Sec. A.
$a = L/10$.

Hammer.	Velocity of hammer before impact v cm./sec.	Initial Impulse mv.	Amplitude of Harmonics (mm.).		
			1st.	2nd.	3rd.
Hollow lead ball, diameter=3·2 cm., wt.=48·5 gm.	43·45	...	1·157	·3770	·1690
„ iron „	43·45	...	1·066	·3445	·1560
„ copper „	43·45	...	·988	·3055	·1560
Brass ball, diameter=2·38 cm., wt.=26·5 gm.	88·40	2342·6	3·5570	·0702	·0243
Brass ball, diameter=5·2 cm., wt.=629 gm.	4·00	2516·0	·0189	·0027	...
	88·40	55623·6	·883	·0918	·0297

Conclusion.

(1) Observations taken support Kaufmann's theory. P. Das's extension of Kaufmann's theory is found to have no agreement with experimental evidence. Calculations made by Mr. S. K. Datta to confirm Das's theory are shown to be wrong.

(2) The striking-point for which the fundamental is maximum has been shown to depend on the ratio of the mass of the hammer and the string. For this striking-point the amplitude of vibration of the string is found to be equal to the displacement at the centre.

(3) The displacement at the centre and the amplitude of the fundamental are found to be proportional to the velocity of the hammer before impact.

(4) The velocity of the hammer before impact remaining the same, the velocity after impact is found to change discontinuously with the striking-point, in agreement with George and Beckett's recent observations.

(5) The area of contact and the nature of the metal of the hammer has a great influence on the strengths of the different harmonics.

(6) When struck at L/n the nth harmonic is not absent, in agreement with the experiments of Hipkins and Kaufmann.

Further investigations regarding the effect of elasticity of the hammer and the string and direct determination of the duration of contact are in progress and will appear in a later communication.

In conclusion, we express our thanks to Mr. Bhupendra nath Bannerji, M.Sc., for helping us in some of our calculations.

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Bengal, India.
July, 1927.

LVI. *On making very Sensitive Helical Springs from Quartz Fibre.* *By* H. D. H. Drane, *M.Sc., Ph.D., Research Laboratory, The Thermal Syndicate Limited, Wallsend-on-Tyne* *.

DIRECT weighing by loading helical springs made of fused quartz is a simple and convenient method, which has been of service notably in studying adsorption phenomena. Most springs used in this way have been made up by bending rod $\frac{1}{2}$–1 mm. or so in diameter approximately to the desired helical shape in an oxygen-fed blowpipe flame, and have had a maximum sensitivity of the order 10^2 cm. per gram, but very much more sensitive springs can be produced. The convenience of this method of weighing, or otherwise of applying a small but accurately measurable force, suggests the use of these springs in many types of physical investigation. The present note describes how springs of perfectly uniform curvature may be produced from quartz fibre with a sensitivity of the order 10^5 cm. per gram. The sensitivity may easily be made greater than this, but for reasons of difficulty in manipulation probably 10^5 cm. per gram represents the practical limit of utility.

The whole process of making a spring need not occupy more than five minutes and is simple to carry out. Four things are required : a supply of quartz fibre, an oxy-coal gas blowpipe, a piece of fused quartz tube of uniform diameter, and a tubular wire-wound furnace in which the quartz tube may be heated to about 1000° C. A length of the quartz fibre is selected (diameters 0·005 cm. and below are suitable) and weighted at one end by a small pellet of wax. The silica tube, which may conveniently be 1–2 cm. in

* Communicated by Lord Rayleigh, F.R.S.

diameter, is softened near one end over an area about 3 mm. square by heating in a small oxy-gas flame. Then, holding the fibre an inch or so from its free end so that this portion projects horizontally, the heated zone of the tube is lowered on to the fibre, keeping the fibre at a right angle to the axis of the tube. Lowering the tube on to the fibre avoids trouble from convection-currents of air which rise from the heated tube. In this manner the fibre becomes attached to the tube by fusion and may later be wound up in the form of a helix. The weighted fibre should not, however, be allowed to hang directly from its point of attachment to the tube where it may easily be broken. The first half turn of the helix should be made very loosely by looping the fibre over the tube with the weight of the wax pellet supported, and only then allowing the pull of the weighted fibre to make this half turn taut. The fibre is then wound up at will, and secured by fusion to the tube near the weighted end in a similar manner to that already described. A small area of the tube 1 cm. or so from the last made turn of the helix is softened, and over this the remaining portion of the fibre is wound. In this process the surplus piece of fibre is usually drawn off automatically by the weight of the wax pellet.

The coiled fibre on its supporting tube is now placed axially into the uniformly heated zone of the tubular furnace and brought to 1000° C., for a few (one or two) minutes. It saves time and is otherwise advantageous to keep the furnace ready at about 1000° C. After heating, the tube and fibre are removed and allowed to cool immediately. The attachments at the end of the fibre are then broken by the finger-nail or otherwise, and the fibre, now in the form of a helix of slightly larger diameter than the tube, may be easily removed. If required, the ends of the spring may be bent about by heating in a very fine jet of coal-gas or hydrogen burning in air.

As an example of the method, coiling fibre $4{\cdot}0 \times 10^{-3}$ cm. diameter on to a tube 0·69 cm. diameter and heating for two minutes at 970° C., gave a fibre spring 1·02 cm. diameter. The sensitivity of this spring was not determined, but a similar spring with twenty turns, 0·88 cm. diameter, extended at the rate of $0{\cdot}33 \times 10^{5}$ cm. per gram, the diameter of the fibre being $1{\cdot}65 \times 10^{-3}$ cm. By altering the conditions of heating, springs of varying diameters may be produced, and it is proposed later to communicate a study of the elastico-viscous behaviour of fused quartz based upon this method.

LVII. *Oscillatory Ionization Currents from Clouds of Cadmium-Oxide Particles.* *By* H. P. Walmsley, *M.Sc.**

[Plate IX.]

THE ionization currents which are obtained from clouds of cadmium-oxide particles dispersed in air by an arc discharge between cadmium electrodes have been described previously [1]. The currents obtained seem to be the sum of two effects [2]. The ionization present on formation of the cloud diminishes with time by recombination, and, as the cloud ages, new ions are produced whose number increases from zero to a maximum and then diminishes. The problem of the present paper is to determine whether the new ions are produced by a continuous process, such as one usually associates, say, with a chemical reaction, giving rise to a smooth ionization curve, or whether the ions are produced by several continuous processes each of which passes through a maximum at a time distinct from the others, thus producing the apparently oscillatory curves which have been described.

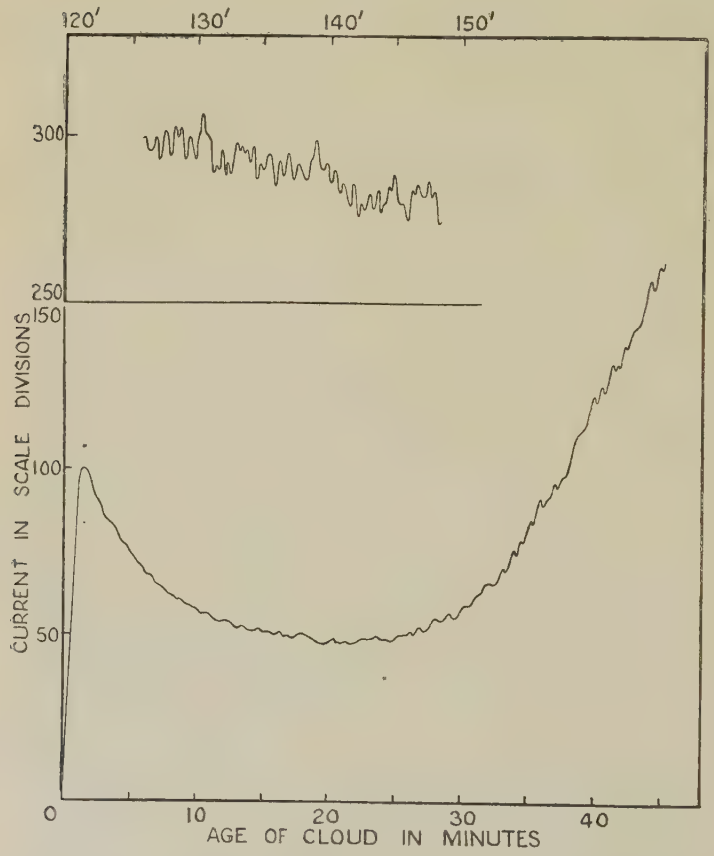
The apparatus employed was similar to the one used before, but instead of measuring the ionization currents by the rate of change of potential of the system, the insulated quadrant of the electrometer was connected to earth through a xylol-alcohol high resistance, and the steady deflexion method was employed. The high resistance increased the electrical capacity of the system and reduced the sensitivity of the apparatus, so that only the currents from the more strongly-ionized clouds could be measured easily. These always gave a curve showing a rise in current strength at some time after the initial sparking in the arc had ceased.

A number of clouds were examined which had been dispersed in dry air free from dust and carbon dioxide. The currents from both positive and negative ions were found to behave similarly. Fig. 1 is an ionization current from the negative charges of a cloud which was dispersed by arcing for 15 seconds. The subsequent variation with time of the deflexions of the electrometer needle are shown in scale divisions. For steady currents 11 scale divisions represent a current of 10^{-13} ampere approximately. In all cases it was found that the ionization curves apparently consisted of a series of kicks following each other rapidly. Their magnitudes varied considerably and the time-intervals between the kicks seemed irregular. Compared with the

* Communicated by the Author.

fluctuations on the weaker clouds, which were measured by the time-rate of the deflexions, those from the denser clouds measured by the steady deflexion method are more numerous, though their mean excursion expressed as a fraction of the total current flowing is considerably less. The diminution in number with the weaker clouds is at least

Fig. 1.



partially accounted for by the method of measurement which averages the effects over the time occupied in obtaining each reading. This not only reduces the number of fluctuations observed, but smoothes them out and tends to eliminate them. Thus, had the currents from the *same* cloud been measured by the two methods, the record by the steady deflexion method should show more numerous and relatively

greater fluctuations in current strength. Provided the fluctuations are not fortuitous, but result from real physical processes such as have been postulated, the decrease in the relative magnitude found for the more strongly-ionized clouds suggests that the number of such processes increases with increasingly denser clouds, and that an ultimate state might be attained in which they were so numerous that the resulting currents would simulate those from a smooth continuous process.

Experimentally, the view that the current is built up of component parts and that each fluctuation indicates the presence of one of them depends upon the extent to which the fluctuations are greater than the experimental errors. Those obtained by the "rate of change" method certainly appeared to be greater than the possible errors. However, as the fluctuations obtained by the more reliable "steady deflexion" method were both more numerous and relatively smaller, the results of a detailed examination of the question are given in what follows.

Photographic Registration of the Currents.

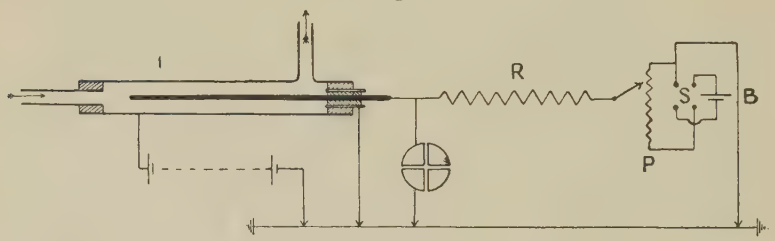
To obtain a more accurate record of the currents, the motion of the electrometer needle was photographed by means of an Edelmann apparatus, where the lateral movements could be registered as an oscillatory line on sensitized paper. A second stationary image of the lamp filament was placed on the paper to provide a fiducial line and to check any movement of the apparatus during an experiment. This image was cut out during an exposure for the first five seconds of every minute. Hence on the record the fiducial line appears broken and forms a convenient time-scale. To avoid errors in numbering the minutes, the half hours were usually distinguished by a break of 15 seconds instead of 5.

Since the width of the sensitive paper is only 6 cm., it is necessary to confine the deflexion of the image to that range; *i. e.*, the potential of the electrometer must be maintained near zero—a favourable circumstance, for the readings thereby reap some of the advantages enjoyed by null methods of working with the electrometer. This was done by applying a suitable potential from a potentiometer to the end of the high resistance whenever the spot of light tended to leave the camera lens. The arrangement of the electrometer circuit is shown in fig. 2. The central electrode of a cylindrical ionization chamber I is connected to the insulated quadrant of the electrometer and to one end of

the xylol-alcohol resistance R. The other end of R is in contact with a potentiometer P to which a Weston cell B is connected in circuit with a reversing switch S. By means of S the potential of P can be made either positive or negative according to whether the currents from negative or positive charges are being measured, without changing connexions. It is also useful when testing the sensitivity of the electrometer.

A Dolezalek electrometer was used at a sensitivity of from 400 to 2000 scale divs. per volt at the camera, according to the purpose of the particular experiment. The sensitivity could be measured on a scale fixed near the camera lens, but usually a record of the deflexion of the needle charged to a known potential was taken on the sensitive paper just before

Fig. 2.



dispersing the cloud. After running the paper a few centimetres, the needle was earthed and the reel stopped when the deflexion again became steady. The speed of the paper was between 100 cm. and 120 cm. per hour. It was cut into metre lengths after exposure for ease in development.

The carrying-out of an experiment with the apparatus is quite straightforward, but, as most of the work has to be done in a darkened room, it is advantageous to make a list of the rather numerous initial operations to be performed, and follow the same routine with each experiment.

Experimental Results.

In fig. 3 (Pl. IX.) are reproduced parts of a record obtained by this method. This cloud was produced by arcing between cadmium electrodes in dry air free from dust and carbon dioxide for 15 seconds. The current rises sharply almost immediately after the dispersal commences and the trace tends to leave the paper. The drop at 0′ 45″, and the subsequent falls which occur at 5′ 15″, 8′ 15″, and

at 13′ 15″, are caused by the alteration of the potential at the end of the high resistance, which was necessary to keep the deflexions on the record. To obtain the ionization curve showing the variation of current with the age of the cloud, it is necessary to cut the film at the time corresponding to the change of potential and raise the fiducial line by an amount equivalent to the change in voltage. If this be the same at each alteration and equal to that employed in determining the sensitivity, the true deflexion, *i. e.* the ionization curve with an arbitrary ordinary scale, is obtained by taking the difference between the curve on the raised section and the trace representing the dead-beat swing of the electrometer needle. This gives a graph corresponding to that of fig. 1.

The photographic records (Pl. IX. figs. 3 & 4) bring out clearly the fluctuating nature of the ionization current. The deflexions in fig. 3 (Pl. IX.) are sharp, and show considerable variations in magnitude over any short interval of time, as well as a general increase as the cloud ages. The latter, however, is not proportional to the deflexion. At $6\frac{1}{2}$ minutes the deflexion is 18·7 cm., at 11 minutes it is 12·3 cm., at 73 minutes it is 37·0 cm., and at 150 minutes it is 38·5 cm. Taking the magnitude of the fluctuations to be the average width between two smooth lines enclosing them, the ratios of the magnitude to the deflexion at these times are 2·30, 2·03, 1·08, and 1·30 per cent. respectively. The ratio thus falls to a minimum and subsequently rises.

Fluctuating currents have been obtained from every cloud examined. They are not wholly due to irregularities in the rate of flow of cloud through the ionization chamber, for they are perceptible when no flow of cloud is taking place and the current is derived from cloud left in the chamber when the flow ceased. The fluctuations are not destroyed when the cloud in the dispersal chamber is continually stirred by a fan, and they are not due to unsteadiness of the electrometer needle. Although this is not perfectly steady as a rule, before the cloud is dispersed, the resulting movements are quite distinct from the fluctuations, as may be seen in fig. 3 (Pl. IX.). The fluctuations, therefore, are due to some property of the cloud.

The Source of the Oscillations.

On the assumption that the ions enter the electric field with the gas stream, there are two possible sources of origin. If at every given instant the ionization throughout the cloud

is homogeneous, the oscillations recorded must represent changes in the density of ionization with time. If, however, there are fortuitous fluctuations in the density of the ions throughout the medium, the oscillations may be due to ions entering the field in clusters or groups. In the latter case the oscillations are occasioned by the flow of cloud past the collecting electrode, whilst in the former case they are not dependent upon the flow.

Density fluctuations may arise in two ways. Even in a homogeneous cloud or a gas, the Brownian motion of the particles causes the number of particles ν in a given volume to fluctuate about the average ν_0 appropriate to the cloud or gas. Writing $\nu/\nu_0 = 1+\delta$ the mean value of the deviation δ is obviously zero, but the mean of its absolute value $|\delta|$ is equal to $\sqrt{2/\nu\pi}$ provided ν is a large number [3]. The fluctuations in density increase relatively as the number of particles per unit volume decreases. Thus, if the number of ions discharging per unit time at the inner electrode of the ionization chamber is sufficiently small, we may expect fluctuations in current strength due to this cause.

Density fluctuations may also arise in the cloud if, during the dispersal process, the matter removed from the neighbourhood of the arc by the air stream from the fan is not subsequently thoroughly mixed with the gas in the cloud chamber. The distribution of density in this case will be somewhat analogous to that which accounts for the appearance of the quivering air over a heated surface. It would cause ions to enter the electric field in clusters or groups.

(*a*) To determine whether the magnitude of the observed fluctuations at any time is of the order to be expected from probability considerations, requires a knowledge of the average number of ions per unit volume of the cloud at that time. Assuming that the ions carry the electronic charge, this number can be calculated from the mean current which will now be proportional to the deflexion of the electrometer needle. Taking the case of the cloud of fig. 3 (Pl. IX.) when 73 minutes old, the current corresponding to a steady deflexion of 37 cm. is $4{\cdot}25\times10^{-12}$ ampere. This current is given by negative charges in the cloud; so the number of electrons passing through the collecting electrode per second is $4{\cdot}25\times10^{-12}/1{\cdot}6\times10^{-19} = 2{\cdot}66\times10^{7}$, which we assume to be the number of ions involved. Inserting this value in Smoluchowski's formula, we find $|\delta| = 1{\cdot}55\times10^{-4}$. The calculated fluctuation from second to second is therefore $2\times1{\cdot}55\times10^{-4}$, *i.e.* 3·1 parts per

10,000 of the normal current strength. The observed fluctuation is about 1·08 per cent.*, so is approximately 35 times greater than that to be expected with the above assumptions from density fluctuations due to the Brownian motion of the ions. If we take into consideration that the time-interval between the successive fluctuations on the trace is more nearly 4 seconds than 1 second, a more appropriate value for the theoretical fluctuation would be $1{\cdot}55\times10^{-4}$, making the ratio 70 instead of 35. In any case, the theoretical value $3{\cdot}1\times10^{-4}$ could hardly have been detected at all in the experiment, as it would be represented by an oscillation about one-tenth of the thickness of the photographic trace itself—much less than the motion due to unsteadiness of the electrometer needle.

Brownian motion might account for the observed fluctuations if the ions carried multiple charges. Reversing the calculation and inserting the value $\frac{1}{2}\times1{\cdot}08\times10^{-2}$ for $|\delta|$ we obtain $\nu=2{\cdot}18\times10^{4}$. The rate of flow of cloud through the ionization chamber was 4 c.c. per second. With a time-interval of 4 seconds the value of ν corresponds to a cloud containing $1{\cdot}36\times10^{3}$ ions per c.c. The average charge per ion $=4\times2{\cdot}66\times10^{7}/2{\cdot}18\times10^{4}=4{\cdot}88\times10^{3}$ electrons. Brownian motion could therefore account for the observed fluctuations if the cloud contained 1360 ions per c.c., each carrying

* If the deflexions recorded were proportional to the current. Since the current is fluctuating, the potential at the electrometer side of the high resistance will be less than that due to a steady current of equal strength. The fluctuations recorded are forced oscillations produced by changes in this potential, and as the free motion of the needle was aperiodic, these will in general be again much less than those due to steady changes in potential of equal magnitude. For example, if the ionization current were given by $i\sin pt$, the fluctuating potential acting on the electrometer would be ultimately given by

$$\mathrm{V}=\frac{\mathrm{R}i}{\sqrt{1+\mathrm{C}^2\mathrm{R}^2p^2}}\sin(pt-\epsilon),$$

where C is the capacity of the system, R the high resistance, and $\tan\epsilon=\mathrm{CR}p$. The motion of the electrometer needle is given by

$$\ddot{\theta}+k\dot{\theta}+\mu\theta\propto\mathrm{V};$$

so if the instrument is calibrated as a voltometer, the readings in volts are given by

$$v=\frac{\mu}{\sqrt{\{(\mu-p^2)^2+k^2p^2\}}}\times\frac{\mathrm{R}i}{\sqrt{1+\mathrm{C}^2\mathrm{R}^2p^2}}\sin(pt-\epsilon-\epsilon'),$$

where $\tan\epsilon'=kp/(\mu-p^2)$.

The steady deflexions ($p=0$) are of course given by $v=\mathrm{R}i$. Thus the actual fluctuations are in all probability considerably greater than the fluctuations recorded. Hence the calculations which follow are of necessity only accurate as regards the order of magnitude of the quantities involved.

an average charge of nearly 5000 electrons. The number of ions, 1360 per c.c., is much smaller than the number of ultra-microscopic particles in the cloud. The latter was probably of the order of 10^7 per c.c. at least. Hence, if the clouds are homogeneous in the sense that the ions in a given volume not taken too small, say 1 c.c., are similar in number, size, etc., to those in any other c.c. on the average, and the fluctuations in current strength are due to density variations in the cloud, some of the ions must be very heavily charged. This seems to be a very improbable state of affairs if the ions enter the electric field with the gas stream.

Some of the particles might, however, aquire large charges if they acted as conductors and acquired a charge from the charged electrode by contact. To account for the effect the charge per ion is $(4{\cdot}88\times10^3)\times(4{\cdot}8\times10^{-10})$ E.S.U. $=2{\cdot}34\times10^{-6}$ E S.U. The outer cylinder of the ionization chamber was charged to 400 volts $=1{\cdot}33$ E.S.U.; hence the average capacity of the carriers involved is $1{\cdot}75\times10^{-6}$ cm. Assuming the carriers to be spherical, this is their radius. They are therefore almost amicrons. On this hypothesis it it difficult to see why so few particles and those amicrons should possess the property of transferring charge. It would be more difficult to explain why their numbers should increase with time to a maximum, and still more to explain why the property should be more marked in dense clouds than in sparse ones, particularly as in the former their chances of disappearance by coalescence would appear to be more favourable.

We can hardly escape these difficulties by postulating larger carriers. We have still to explain the increase in efficiency with time, and, in addition, some explanation would be required of why the fluctuations did not obey Smoluchowski's formula, for we can only increase the size of the carriers by diminishing their number.

(*b*) The view that the oscillations are caused by the ions entering the electric field in clusters or groups owing to imperfect mixing of dispersoid and the medium seems equally untenable. The fluctuations persist whether the fan in the cloud chamber is rotating slowly or rapidly, or not rotating at all, during the whole life of the cloud after dispersal. Apparently they cannot be destroyed by mechanically mixing the cloud. Even if the mixing were imperfect initially and the cloud not disturbed by the fan, the Brownian motion of the particles would tend to produce a

uniform distribution as the cloud aged [4]. We should therefore expect the magnitude of the fluctuation to diminish with time. Actually the oscillations grow in magnitude as the cloud ages, and although the fluctuation diminishes for a time, it passes through a minimum and afterwards increases.

The frequency of the oscillations lends no support to the theory of imperfect mixing. For simplicity, suppose we had employed a parallel plate type of ionization chamber and consider only the flow of ions. Ions of mobility κ in a plane perpendicular to the direction of the flow are driven by the field to the collecting electrode, and are spread out over a distance $y = Q/\kappa V$ in the direction of flow, where Q is the rate of flow into the ionization chamber and V the potential gradient in the field. Hence, if all the ions have the same mobility, the groups crossing this plane will strike the collecting electrode as groups in which the distribution of ions is unaltered [5] and the resulting ionization current will be oscillatory. If, however, the groups contain ions of different mobilities, the field will sort each group containing n different mobilities into n groups, each of which takes a different time to cross the field. Thus, if g such groups enter the field in unit time and are distributed at random in the gas stream, we may expect ng groups of ions to strike the collecting electrode per unit time, provided we neglect the possibility of a slowly-moving group of ions from one cluster striking the electrode simultaneously with a more mobile group from a later cluster. Thus the g groups would give rise to ng fluctuations per unit time. I have seldom found more than 7 or 8 fluctuations per minute in any cloud, using a flow Q of 250 c.c. per minute. The maximum value of ng, therefore, is 32 per litre. As the work in a previous paper [1] has shown that n is probably large, it follows that the number of groups or clusters, if any, must be very small *.

From their mobility, the ions have been shown to be

* This argument fails, of course, if the mobilities of the particles are so close that the dispersive action of the field is insufficient to separate the groups. In this case the effect of the field would be to increase the volume occupied by each cluster before it entered the ionization chamber. The fluctuations would now indicate a sparse distribution (32 per litre) of locations where the volume density of electrification was relatively great. It is difficult to see how such a state could develop in the cloud and then be maintained for long periods against the self-repulsion of the charges. A system of doublets might overcome the question of electrostatic stability, but would lead to consequences for which there is no experimental justification at present.

charged particles in the cloud[1]; so an irregular distribution of ions such as would exist on the theory of imperfect mixing suggests an irregular distribution of particles. This distribution of density will become more marked as the volume of the cloud examined diminishes. Observations of the particles in clouds produced from an arc have been made by Whytlaw Gray, using an ultra-microscope, upon a volume of $1{\cdot}27 \times 10^{-6}$ c.c.[6] This should be eminently suitable for the purpose. The individual counts of the number of particles in successive volumes of cloud of this size give no indication whatever of clustering. As these counts presumably are typical of arc clouds, it is evident that successions of numbers much higher and much lower than the average were not found. The fluctuation of the individual counts about the mean seems no greater than is to be expected from the probability variations in a homogeneous cloud.

Collecting the evidence for imperfect mixing, the frequency of the oscillations shows that the resulting clusters are few in number. They have not been observed in the ultra-microscope, and they are not destroyed by diffusion or mechanical agitation. The conclusion that imperfect mixing does not account for the oscillations seems inevitable. The clouds are homogeneous, therefore, in the sense that the contents of one c.c., say, are similar to the contents of any other c.c. within the limits imposed by statistical fluctuations. It is equally certain that the current is not wholly carried by ions possessing a large average charge.

(*c*) It is possible that the oscillatory current is the resultant of two effects. The main current may be carried by ions with small charges whose density varies relatively slowly with time, giving rise to a smooth curve, and the fluctuations fig. 3 (Pl. IX.) are superposed upon this by ultramicrons acting as carriers of large charges. There is an upper limit to the charge which can be acquired by an ultra-micron by contact with the charged boundary of the electric field. This is determined by the dimensions of the tube carrying the gas stream from the cloud chamber to the field. With a steady flow the particles in motion in the stream slowly settle under gravity. Assuming them spherical, Stokes's law gives the relation between the velocity of fall and their radius a. The tube is horizontal. Hence, if the time taken by a particle to fall through a distance equal to the diameter of the tube is less than the time

required for it to pass through the tube, it will settle on the wall of the tube, and no particles of that size will enter the field—provided we neglect the growth by coalescence during the passage of the particles through the tube. Taking the axis of y vertically downwards and that of x horizontal, with sufficient accuracy

$$\dot{y}=v=2/9\,.\,a^2g\rho/\eta. \qquad \text{(Stokes's Law.)}$$

Assuming the particle moves with the stream, the velocity

$$\dot{x}=2Q(\alpha^2-r^2)/\pi\alpha^4,$$

where Q is the flux and α the radius of the tube.

Substituting $\quad r=\alpha-vt,$

$$\dot{x}=2Qvt(2\alpha-vt)/\pi\alpha^4,$$

and $\quad x=2Qvt^2(\alpha-\tfrac{1}{3}vt)/\pi\alpha^4,$

the particle hits the bottom of the tube when $\dot{x}=0$; *i. e.*, $vt=2\alpha$ at a distance

$$x=8Q/3\pi\alpha v.$$

If L be the length of the tube, the particle will not leave it unless

$$v\leqq 8Q/3\pi\alpha L;$$

i. e., $\quad a<(12\eta Q/\pi\rho g\alpha L)^{\frac{1}{3}}.$

Inserting the experimental values for the case of the lighter trace of fig. 4 (Pl. IX.),

$Q=3{\cdot}12$ c.c./sec., $L=120$ cm., and $\alpha=0{\cdot}25$ cm.,

no particles will enter the field if $a\leqq 2{\cdot}95\times10^{-4}$ cm. To obtain an appreciable proportion of the number of particles entering the tube, a must be considerably less. With a value $a=2\times10^{-4}$, little more than one-third of the particles reach the field *.

The upper limit to the charge carried across the field by a particle is $2{\cdot}95\times10^{-4}\times500/300=4{\cdot}9\times10^{-4}$ E.S.U. For steady currents the charge ($\int idt$) collected by the electrode

* The order of magnitude of these quantities agrees with the experimental values found on the previo us paper. When the cloud of fig. 3 of that paper was $2\frac{1}{2}$ hours old, the radius of the slowest-moving ions, estimated from their mobilities on the assumption that they carried the electronic charge, was $1{\cdot}76\times10^{-4}$ cm. The values of Q, a, and L were substantially the same as those above, and the ions must have been present in appreciable numbers to have been detected.

is proportional to the area enclosed by the trace. The sensitivity was 2040 mm./volt, the high resistance $1{\cdot}05 \times 10^{11}\omega$, and the paper was run at a rate of 20 mm./min. Hence 1 sq. mm. on the paper (which is 6 cm. wide) represents a charge of $3{\cdot}2040 \times 1{\cdot}05 \times 10^{11}$ coulombs $= 4{\cdot}2 \times 10^{-5}$ E.S.U. The charge carried by the particles is represented, therefore, by an area of 12 sq. mm. on the paper. It is evident from the record that, even on these assumptions which overestimate the effect of a solitary particle, it would be necessary for numbers of them to act together to account for the oscillations. Thus, whether the current is wholly due to the ions carrying small charges, or to heavily-charged ions alone, or to a mixture of both, each fluctuation results from the joint contributions of many ions to the current.

Since the current as a whole is due to ions which have appeared in the cloud as it ages, the magnitude of the fluctuations conforms with the theory that the disruptive process to which they are due is not continuous, but consists of a series of component continuous processes, each of which gives rise to an ionization current which passes through a maximum occurring perhaps at a characteristic time in the life of the cloud. On this hypothesis the superposition of these components would produce the fluctuating current observed, and the number of components would equal the number of fluctuations observed.

Evidence has been given previously that the current as a whole is due to charged particles which have arisen from the disruption of unstable aggregates produced in the cloud during the process of coalescence of primary particles formed by the arc[2]. From the present results it seems a legitimate deduction, that each component of the current is due to the disruption of a specific group of unstable aggregates, and that, as the cloud ages, the disruptions in individual groups become successively dominant. That the number of these groups is so large, being equal, when the field does not separate the resulting ions into distinct groups, to the number of the fluctuations, need occasion no surprise. If the particles of a cloud in which the primary particles are coalescing to form aggregates are analysed into groups according to the number of primaries contained in each particle, we expect, *a priori*, to obtain a complex distribution, for both the number of groups and the number of particles in each group would be expected to change as the cloud aged. If, further, certain of the unions between primaries in the aggregates are unstable and possess something of the nature of an average life, we could hardly expect an analysis

into groups of the unstable particles to be less complex. The results of the experiments therefore lead to the conclusion that, from a study of the fluctuating ionization currents, we may hope to obtain ultimately an analysis and a life-history of at least the unstable aggregates in clouds. As this would be of some importance in the study of disperse systems in gases, further experiments are being undertaken to check the accuracy of these deductions.

Summary.

The ionization currents from cadmium-oxide clouds dispersed from an arc have been registered photographically, using the steady-deflexion method of measuring currents. They are found to fluctuate rapidly. On experimental grounds, and by comparison of the magnitude of the effect with what would be expected from the theory of chance fluctuations it is concluded that the observed fluctuations represent time-changes in the density of ionization throughout the cloud. As the currents investigated arise from the disruption of unstable complex particles which have been produced in the cloud during the process of coagulation, it is suggested that each fluctuation is due to a group of unstable complexes which apparently possess the same average life. The current due to a group is conceived to be zero initially, increase with time to a sharp maximum (corresponding to the fluctuation) at the mean time of disruption of the group, and afterwards to steadily diminish. The superposition of currents corresponding to successive groups of unstable particles gives the fluctuating current which is observed.

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(1) Walmsley, Phil. Mag. (7) i. p. 1266 (1926).
(2) Walmsley, Phil. Mag. (7) iii. p. 587 (1927).
(3) Smoluchowski, Boltzmann *Festschrift*, p. 626 (1904); *Ann. d. Phys.* xxv. p. 205 (1908).
(4) Smoluchowski, *Phys. Zeit.* xvii. p. 557 (1916).
(5) Townsend, 'Electricity in Gases,' p. 134 (Oxford, 1915).
(6) Whytlaw Gray, Proc. Roy. Soc. A, cii. p. 600 (1923).

Erratum.—Fig. 3 (Pl. IX.) for 45′ read 145′.

LVIII. *Some Experiments on the Auto-Electronic Discharge.*

By N. A. de Bruyne. (Communication by the Staff of the General Electric Company, Limited, Wembley.)

[Plate X.]

Summary.

A clean tungsten cathode of small diameter was produced by burning out a tungsten filament. The auto-electronic currents from this cathode in a high vacuum were reproducible. The currents were decreased by hydrogen and still more by air ; they were increased by coating the cathode with barium. It is concluded that auto-electronic currents are not due to gas, but that they depend on the nature of the cathode in somewhat the same way as the thermionic emission.

Lilienfeld discovered that if a cold cathode is subjected to a sufficiently high electric field, currents of the order of microamperes flow from it ; such currents he terms auto-electronic. Recent workers on the subject include, besides Lilienfeld himself *, Millikan and Eyring †, the staff of these laboratories ‡, Rother §, and del Rosario ‖. Of these, Lilienfeld and ourselves connect the magnitude of the currents with the nature of the cathode, and produce evidence that the currents are the greater from the more electro-positive cathode. Del Rosario considers that the whole effect is due to residual gas. The experiments here described were directed to decide between these alternatives.

Experimental Details.

In order to investigate the effect of gases on the discharge, it is obvious that the cathode must be as clean and gas free as possible. For this reason the cathode was formed in a high vacuum by burning out a tungsten filament at a high current density. This produced two smooth fused ends,

* J. E. Lilienfeld, *Zeit. f. Phys.* xv. p. 46 (1923) ; *Phys. Zeit.* xxiii. p. 507 (1922).

† R. A. Millikan and C. F. Eyring, Phys. Rev. xxvii. p. 51 (1926). A preliminary note appears in Phys. Rev. xxii. p. 525 (1923).

‡ Research staff of the G. E. C., Ltd. (B. S. Gossling), Phil. Mag. l. p. 609 (1926).

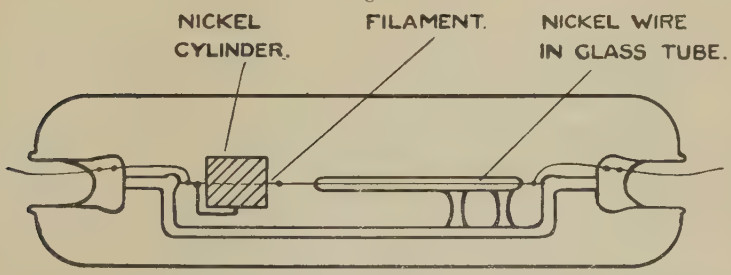
§ F. Rother, *Ann. d. Phys.* lxxxi. p. 317 (1926). This paper contains a bibliography of previous work.

‖ C. del Rosario, J. Franklin Soc. cciii. p. 243 (1927).

one of which was used as a cathode. The form of discharge-tube used is shown in fig. 1. One end of a straight tungsten filament was spot welded to the bottom of the closed end of a concentric nickel cylinder. The other end of the filament was spot welded to a long nickel electrode encased in a glass tube to increase its rigidity. The electrodes were assembled on a framework consisting of two lamp pinches joined by a glass rod; the completed assembly was then slid into a glass tube and sealed in.

The tubes made in this way were baked at 400° C. for an hour; the nickel cylinder was heated to bright red heat by an eddy-current heater for twenty minutes. The filament, which before sealing-in had been thinned down locally by a tiny flame, was lit at bright white heat for half an hour. It was then burnt out by suddenly raising the current; a

Fig. 1.



slow increase of current always resulted in a tangled filament. Fig. 2 (Pl. X.) shows a silhouette of a cathode formed in this way, and fig. 3 (Pl. X.) shows the brilliant lustre produced.

The high-tension supply (up to 20,000 volts) was supplied by a full-wave thermionic rectifier, with smoothing condenser and electrostatic voltmeter. The voltage control was carried out by a tapped auto-transformer, and was only variable in rather large steps.

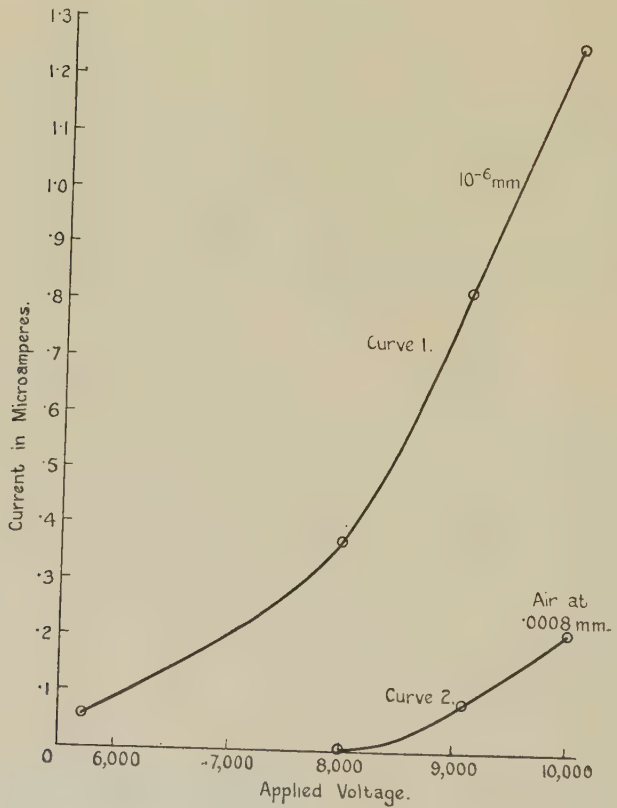
To guard against electrical leaks an earthed guard-ring was clamped round the discharge-tube. The fact that no current was ever observed to pass, even at 20,000 volts, when the nickel cylinder was made the cathode showed that there was no measurable leakage.

The current was measured with a Tinsley portable reflecting galvanometer of sensitivity 35 mm./microamp.

The pumping equipment consisted of a three-stage glass diffusion-pump connected through a reservoir to the central

backing system. Next to the diffusion-pump was a mercury cut-off, then a MacLeod gauge, liquid-air trap, ionization-gauge, and the discharge-tube.

GRAPH 1.



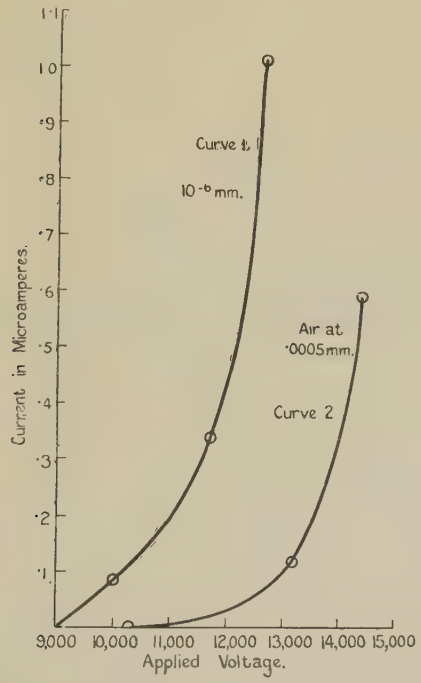
Results obtained.

It was found possible to obtain reproducible characteristics provided that the voltage was not carried too high, in which case a bright star could be seen momentarily on the cathode and a new characteristic was obtained. This star evidently signifies the tearing-off of a particle from the cathode surface. Curves 1 of graphs 1 and 2 show the characteristics of two different tubes when the pressure was less than 10^{-6} mm. Each point is the mean of a number of observations with ascending and descending voltages. The curves 2 are those

obtained when air was admitted ; they were also reproducible; pumping the air out did not restore the original characteristic.

A similar but less marked effect was found when hydrogen was admitted. The hydrogen was purified by passing electrolytic hydrogen over two KOH towers, red-hot copper, two KOH towers, six P_2O_5 towers, and red-hot chromium, in that order. Graphs 3 and 4 show the results with hydrogen.

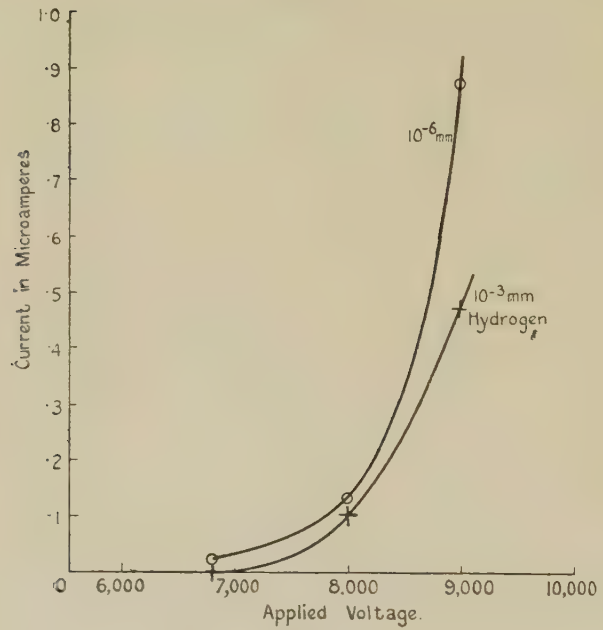
Graph 2.



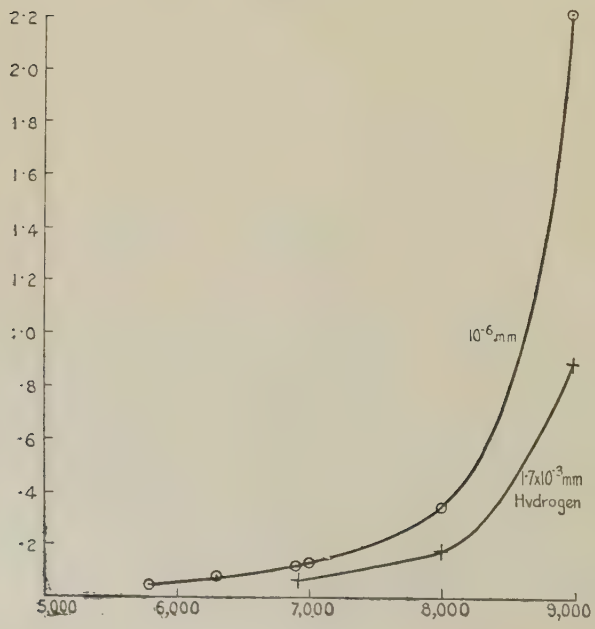
N.B.—The voltages for this characteristic were extrapolated from the primary voltage, which had been calibrated below 10,000 v. against the electrostatic voltmeter.

The inside of the nickel cylinder of a discharge-tube was coated with barium azide and baked *in vacuo* at 400° C., leaving a deposit of barium on the inside of the cylinder. The filament was then burnt out and the characteristic 1 in graph 5 was obtained. The nickel cylinder was heated up by the eddy-current heater and a positive potential of 100 volts was applied to the burnt-out filament; the barium

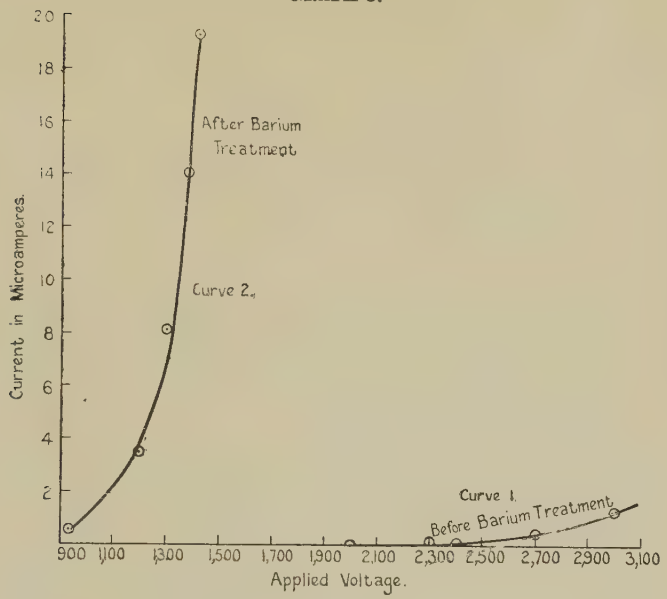
GRAPH 3.



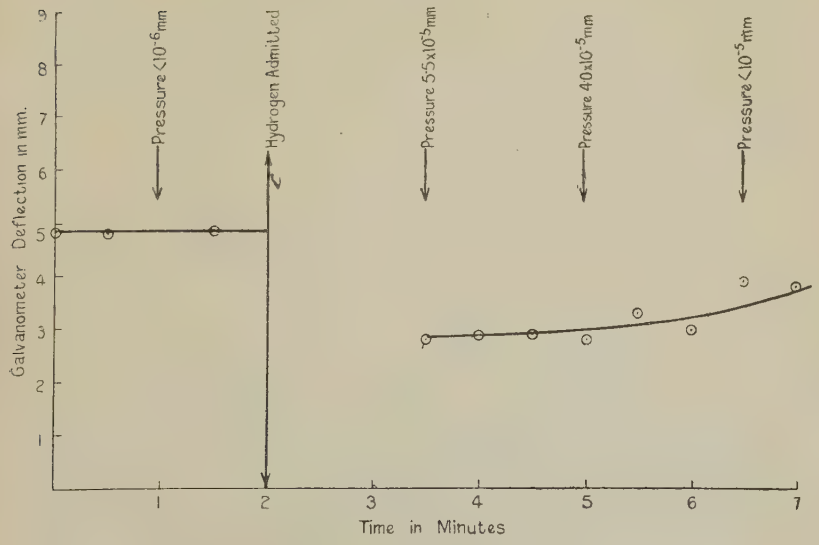
GRAPH 4.



GRAPH 5.



GRAPH 6.



was vaporized and a glow-discharge set in, the positive barium ions being attracted to the filament. The characteristic 2 was obtained after this treatment; it was not reproducible. The barium coating increases the emission, but is evidently torn off by the discharge.

The gas-pressures marked in the graphs were taken immediately after the characteristic had been obtained. Actually the pressure decreased continuously, as graph 6 shows, due to the disappearance of the gas in the discharge.

Discussion of Results.

It appears, then, that the effect of the agencies studied upon the auto-electronic currents is of the same kind as their effects upon thermionic emission at a given temperature.

This conclusion is consistent with the theory of Schottky *, which, however, seems not to explain why the auto-electronic current should be almost independent of the temperature while the thermionic current varies so rapidly with it. It is not consistent with del Rosario's theory that auto-electronic currents are due to traces of residual gas.

The author wishes to thank the Director of the Research Laboratories of the General Electric Company for granting permission to carry out this work at the laboratories, and to Miss M. Crowe for her assistance. He also wishes to express his great indebtedness to Mr. B. S. Gossling, whose interest and helpful advice made this work possible, and in particular for suggesting the process of burning out a filament to obtain a clean surface.

LIX. *On the Effect of Constrictions in Kundt's Apparatus and the End Corrections of a Partially-stopped Tube.*

By Eric J. Irons, *B.Sc.*, *East London College* †.

[Plate XI.]

1. *Introduction.*

At the suggestion of Professor C. H. Lees ‡ experiments have been made to determine the effect on the distribution of nodes and loops of introducing diaphragm constrictions in Kundt's sound apparatus.

* W. Schottky, *Zeit. f. Phys.* xiv. p. 63 (1923).

† Communicated by Prof. C. H. Lees, D.Sc., F.R.S.

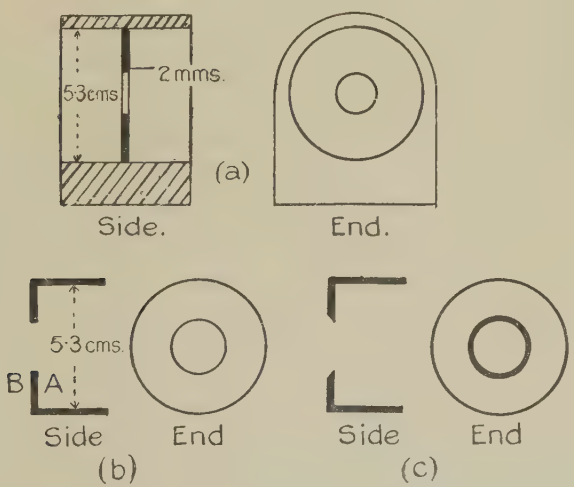
‡ To whom I am indebted both for facilities for carrying out this work and for counsel during its progress.

The method of investigation has been further applied to the problem of the end corrections of a tube fitted with caps containing holes of different radii, and the results are herein described.

2. *Apparatus and Preliminary Results.*

As a source of vibration a hollow cylindrical bar of brass 110 cm. long and 1 cm. external diameter was used. It was so clamped at its centre between two triangular prisms of wood that a definite node was formed at that point. A firmly fitting circular cork disk was attached to that end of the bar which protruded into the sound-tube, and the other end of the bar was weighted so that it balanced about its centre.

Fig. 1.



Because of the facility with which it formed into figures without special precautions as to dryness, cork dust (obtained by sifting through a fine copper mesh) was chosen as a powder to indicate the positions of the antinodes.

Preliminary experiments showed that it was possible to obtain dust figures in an open tube, in a tube fitted with a stop covered by a considerable thickness of felt, and also on a lath placed along the axis of the tube. The figures in the last instance did not admit of such easy measurement so that the device was not subsequently used.

The constrictions and caps were of aluminium and of the shapes shown in fig. 1. The former were designed to carry a sound-tube on either side, thus forming a "single tube with a constriction." The tube further from the vibrating rod was furnished with a solid movable stop, and will be referred to as the "stop tube" in contradistinction to the "vibrator tube" into which the end of the rod protruded.

With the constrictions two types of experiments were carried out.

For the first type the *modus operandi* was to adjust the distance from the constriction to the end of the rod (by moving both the tubes with the constriction), and to the stop (by moving the stop itself) until *good figures* were obtained in both tubes. The tubes were then cleaned, relaid with dust, and placed in their former positions. If good figures were obtained by stroking the rod once, or at most twice, with a resined duster, then the positions of the antinodes were recorded.

The second type of experiment was designed to determine the positions of the loops for a given position of the stop; in some instances a considerable amount of stroking was required to produce any semblance of figures in the tubes.

With the caps the adjustment followed the lines of the first type of constriction experiment, except that it was much simpler, there being but one length (viz. the distance between the cap and the end of the vibrating rod) to alter. This was effected by sliding the tube in or out relatively to the rod. Care was taken that the cap projected well over the end of the bench supporting the apparatus and was removed from any near object likely to give rise to a reflected wave.

3. *Results.*

The results (the means of a large number of observations) are best described by reference to the figures.

I. Constrictions.

First Type of Experiment. (See fig. 2.)

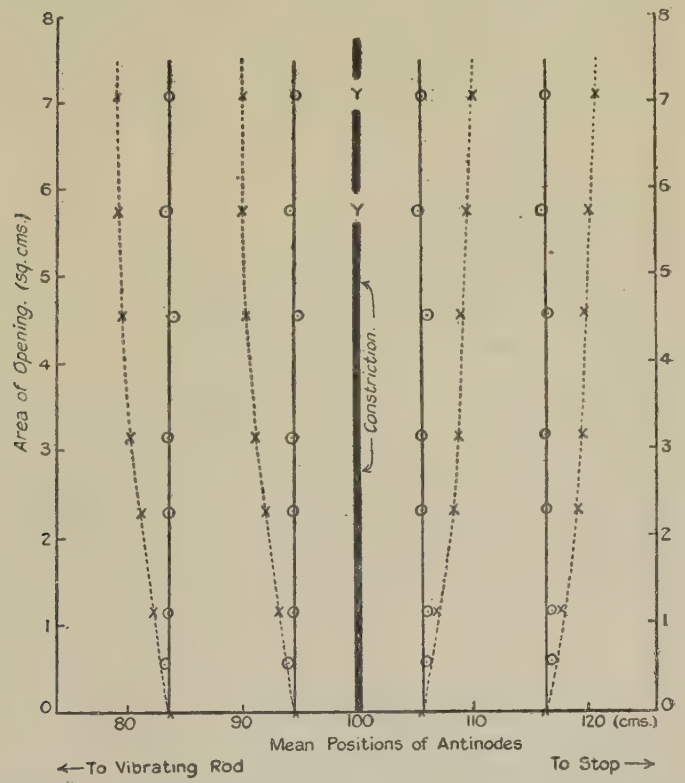
In the figure the area of the opening is plotted as ordinate against the positions of the antinodes as abscissa—the constriction being at 100,—and the results correspond to a half wave-length of 10·8 cm.

The results occur in two groups, viz. :—

Group A (marked ⊙) in which there is no displacement of the antinodes, the constriction appearing to form a node whatever the area of the opening.

For results of this type the distance of the stop from the constriction approximated to an integral number of half

Fig. 2.—Internal Area of Cross-section of Tubes = 17·3 sq. cm.



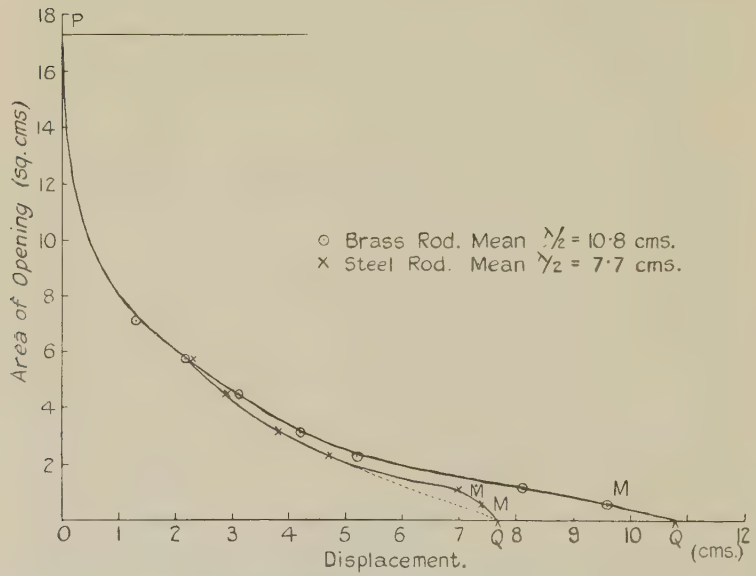
wave-lengths, while the distance of the end of the vibrating rod from the constriction (*i. e.* a node) exceeded in general an integral number of half wave-lengths by about a centimetre.

Group B (marked ×). The antinodes are symmetrical about the constriction but are moved out from it in both tubes.

Here the difference between the distance of the stop from the constriction and a whole number of half wave-lengths was comparatively large, and tended to increase with the aperture as it (the stop) was always at a distance of $\lambda/4$ (λ is the wave-length of the disturbance in the tube) from the nearest antinode in the tube. No general rule could be found for the position of the end of the rod.

Fig. 3 indicates the extent of the displacement for the various openings for Group B. If it be assumed that an antinode would occupy the position of the constriction were it removed, then the point P is fixed as a point of no displacement. As the area of the opening decreases the

Fig. 3.—Internal Area of Cross-section of Tubes=17·3 sq. cm.



nodes on either side of the partition approach it, and when the partition is solid the nodes coincide with it. It follows that the point Q is also fixed, since the distance between the two antinodes which are adjacent to the constriction in the two tubes is half a wave-length.

The points marked M represent the mean displacement for results of both groups (see note (i.) below) ; in consequence the variation is probably better represented by the dotted line for the steel rod (see below). With this rod results corresponding to Group B were not noted with an aperture of 7·1 sq. cm.

The following afford further explanation of fig. 2 :—

(i.) For the constriction having an opening 0·55 sq. cm. in area the accuracy of the experiments does not justify the division of the results into groups.

(ii.) Figures for the opening of area 0·55 sq. cm. indicate that results of Group B are probably present, but indistinguishable from those of Group A.

(iii.) In the places marked "Y" in experiments of Group B it was noted that the dust near the constriction was disturbed.

(iv.) With a constriction of aperture 9·08 sq. cm. the results were not sufficiently consistent to justify their classification at all—due, probably, to the fact that the apparatus acted as a single resonator.

By substituting for the brass rod one of steel having the same dimensions, figures were obtained in the tube with an antinodal distance of c. 7·7 cm. In general the results were similar to those already described for the brass rod. The relation between the area of the opening and the displacement in results of Group B for this rod is also shown in fig. 3.

An experiment with a diaphragm having an opening of diameter 0·3 cm. was tried with this rod. With prolonged stroking, faint figures, which were capable of fairly accurate measurement, were obtained in the stop tube. In the vibrator tube the antinodes were destroyed, and the dust was first carried along and deposited in heaps at the nodes in the manner described by Barton *, while finally a transverse ring of fine dust was formed there. This effect appears to be illustrated diagrammatically in Tyndall's 'Sound' †, to which the reader is referred for an interesting account of Kundt's experiments.

Second Type of Experiment. (See fig. 4.)

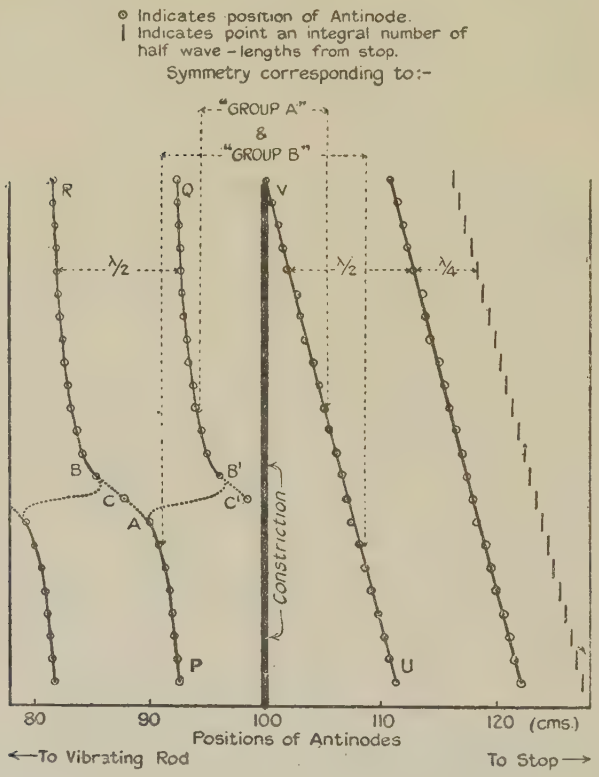
The first type of experiment having demonstrated the positions of *good* and easily obtained figures, it was thought desirable to investigate the positions and modes of production of any other figures that could be obtained. To this end experiments with any one constriction were made in which the position of the stop was fixed and that of the end of the vibrating rod varied, and *vice versâ*. It became

* 'Text-book of Sound,' p. 369. (Macmillan & Co.)
† Fourth Edition, 1883, p. 213. (Longmans Green & Co.)

apparent that whether the stop was fixed at a distance of an integral number of half wave-lengths from the constriction or not, the position of the end of the vibrating rod played such a very minor part in the production and position of figures that its influence could well be neglected compared with that of the stop.

The curves obtained with the brass rod for a constriction

Fig. 4.



having an opening of 3·1 sq. cm. are shown in fig. 4, and illustrate the characteristics of similar results obtained with larger and smaller openings. In this instance the position of the end of the vibrating rod was fixed at 110·2 cm. from the constriction, and that of the stop was altered progressively by steps of half a centimetre.

It should be noted that where the dust figures were too

near the constriction for complete formation or convenient measurement, the positions of the antinodes they represent were determined by adding or subtracting half a wave-length from the neighbouring antinode in the same tube.

The positions of the antinodes (marked ⊙) in the stop tube are seen to depend on the position of the stop, which was at an integral number of half wave-lengths from the points marked |.

In the vibrator tube the results varied considerably with the area of the aperture in the constriction. For the example illustrated by fig. 4 it is seen that a movement of the stop through a centimetre was sufficient to cause the antinodes to move from A to B or B′. By moving the stop through half a centimetre from the position corresponding to A, indifferent figures were obtained indicating antinodes at C and C′.

With constrictions having *small* openings the curve was of the same form, but the shift A to B′ was much less and no intermediate positions such as C could be detected—the sequence of events being represented by PAB′Q (for a considerable portion of its length an almost straight line parallel to the constriction and at a distance approaching to a quarter of a wave-length from it), rather than PABR (see fig. 4). In these instances the dust figures in the vibrator tube were good, while those in the stop tube were unsatisfactory over the straight portion of PAB′Q.

With constrictions having *large* openings the line PABR appeared to be continuous, and became straighter, each point in it tending to be at a distance of a wave-length from the corresponding point in UV—a condition that would be completely realised in the absence of any constriction.

The shapes of PAB′Q and UV are such that there are two positions for which the figures in the two sound-tubes are symmetrically placed with respect to the constriction. During experiments of the second type it was noted that the figures in these cases were both easier to obtain and more clearly defined than usual, and, in fact, corresponded to those already measured in the first type of experiment.

II. Caps.

The fact, already noted, that it is possible to obtain dust figures using an open tube led to experiments being performed to determine the effect of placing on the end of the tube caps having openings of different apertures.

This method of investigation affords a convenient means of estimating "end corrections." The value of the half wave-length of the disturbance in the tube ($\lambda/2$) being known from the antinodal distance, and the distance of the antinode nearest the end from that end (c) being measurable, it follows that the end correction is ($\lambda/2-c$). In practice the positions of some six antinodes were measured, and a mean position of the end antinode was calculated.

Experiments of a more general nature on end corrections and allied problems are in progress, and it is hoped that the results of these will be published in due course ; it is thought well, however, to introduce here the results obtained by the Kundt's tube method.

The caps were 2 mm. thick, and the first experiments have been carried out with those of the type shown in fig. 1 (b). The question arose as to the position of the "end of the tube," *i. e.* whether measurements should be made from inside the cap at A or outside the cap at B (see fig. 1 (b)). To obviate this difficulty caps of the type shown in fig. 1 (c), having the edge of the aperture bevelled at 45°, are now employed and measurements are made from the inside edge. The effect of this alteration on the vibration at the end of the tube is described later.

In addition, experiments have been performed using a flange * 120 cm. in diameter fitted over and flush with the caps.

In order to increase the range of wave-lengths a two metre vibrating rod of brass was employed. This rod when clamped at its centre was capable of emitting both its fundamental and first overtone giving rise to antinodal distances in the tube of approximately 19·6 and 6·5 cm. respectively. In general the overtone was generated when the rod was stroked near its centre and the fundamental

* By the electrical analogy of Rayleigh a very rough measure of the deviation of this flange from an "infinite" flange may be obtained.

Remembering that the resistance between *spherical* equipotential surfaces of radii r_1 and r_2 is $(1/4\pi).(1/r_1-1/r_2)$, it follows that, assuming the waves diverge in *hemispherical* form, the resistance between a hemisphere at the end of the tube of radius r_1 and the edge of the flange of radius r_2 is $(2/4\pi)\ (1/r_1-1/r_2)$. Further, between the edge of the flange and infinity the resistance may be written as $(1/4\pi).(1/r_2-1/\infty)$, making a total of $(2/4\pi)\ (1/r_1-1/2r_2)$ for a small flange and $(2/4\pi).(1/r_1)$ for an infinite flange ($r_2=\infty$). In round numbers for the case in question, $r_1 = 2{\cdot}5$ and $r_2 = 60$ cm., so that the actual resistance is measured by $\cdot196/\pi$ and the resistance of an infinite flange by $\cdot200/\pi$.

when it was stroked towards its end. In many cases the effect of the overtone in the tube was somewhat difficult to eliminate, because its striæ joined those due to the fundamental on one side or the other to form a composite figure. Satisfactory results with the fundamental were obtained using caps of the first type and are described below.

Fig. 6.—Internal Area of Cross-section of Tube=18·9 sq. cm.

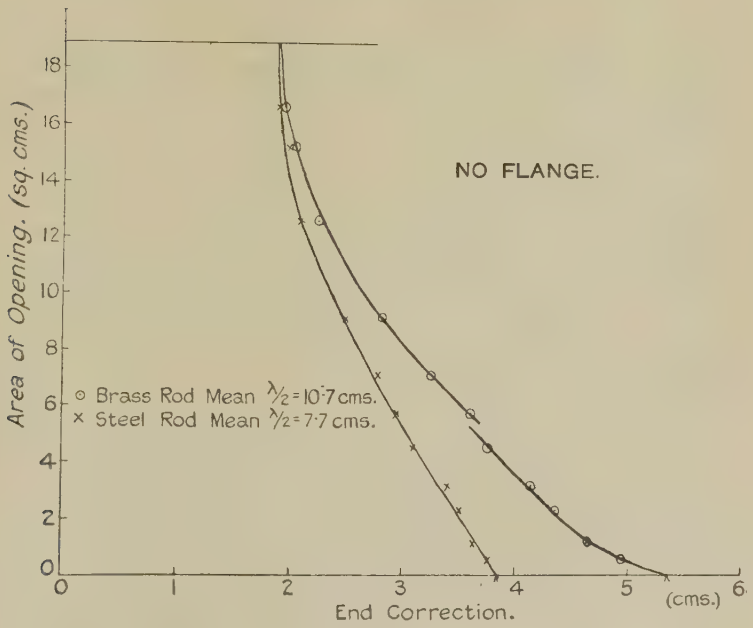


Fig. 5 (*a*) (Pl. XI.) shows the effect obtained in a particular instance in which antinodes due to the two notes are seen to alternate down the tube.

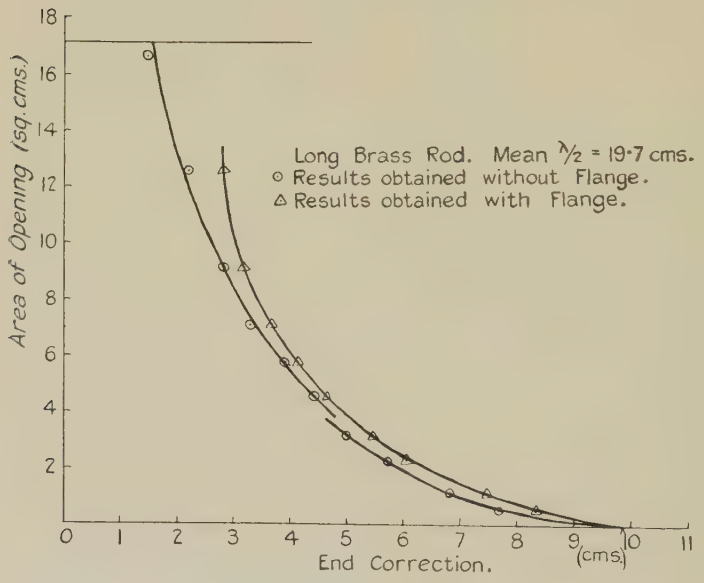
The other photographs of fig. 5 (Pl. XI.) show the tube after an experiment with, and the removal of, a cap having an aperture of 0·55 sq. cm., and demonstrate the difference in the appearance of the dust—noted especially with small aperture caps—according as the cap is bevelled (*b*) or plane (*c*). In the former instance the dust is violently agitated near the end while in the latter the antinode is well formed.

There follow graphs setting forth the means of a number of results in good agreement obtained for various combinations of cap and vibrating rod. Distances are measured

from the end of the glass sound-tube in each case (*i.e.* from A in fig. 1 (*b*)), and by "end correction" is denoted the distance from the end of the tube of an external point which is half a wave-length from the last antinode inside the tube.

The curves for the brass rods and unflanged caps (figs. 6 and 7) appear to consist of two parts according as the area of the opening of the cap is relatively small or great. In

Fig. 7.—Internal Area of Cross-section of Tube=17·1 sq. cm.



what follows attention will be confined to the results shown in fig. 7 which correspond to the largest wave-length used.

Considering the *unflanged* caps: when the holes are *small* the space between the cap and the nearest node in the tube may be considered as a resonator whose frequency N is proportional to $\omega^{\frac{1}{2}}/Q^{\frac{1}{2}}$ *, where ω and Q are the area of the opening and the volume of the resonator respectively. In these experiments, N being constant and the resonator

* See, *e. g.*, Lamb, 'Dynamical Theory of Sound,' pp. 267–68 (Arnold & Co., 1925.)

cylindrical, it follows that $(r/d)^{\frac{1}{2}}$ should be constant, where r is the radius of the opening and d $\{=\lambda/4-(\text{end correction})\}$ is the distance of the nearest node from the cap.

The following table shows the variation of $(r/d)^{\frac{1}{2}}$ for the small-holed caps :—

r (cm.).....	0·42, 0·60, 0·85, 1·00,	1·20
$(r/d)^{\frac{1}{2}}$	·443, ·447, ·455, ·455,	·471

From this it would appear that for holes in the caps up to a radius of 1 cm. the system may be regarded as a resonator of the type indicated, although theory supposes the wave-length to be large compared with the linear dimensions concerned.

The *flanged* caps for *small* openings do not follow this rule so well but it may be noted that there is a variation of about 12 per cent. in the value of $(r/d)^{\frac{1}{2}}$ over the whole range. With *flanged* caps and *large* openings, however, the product end correction times radius of hole in cap is a constant, as appears from the following table :—

Radius (cm.)	2·0,	1·7,	1·5,	1·35,	1·2,	1·0
End correction × Radius...	5·56,	5·36,	5·46,	5·55,	5·57,	5·43

It remains to discuss some results for the end correction of an open tube as ordinarily understood. For notes corresponding to half wave-lengths of 6·6, 7·7, 10·7 and 19·7 cm., values of the end correction corresponding to 0·57, ·62, ·58 and ·64 times the internal radius of the glass tube were obtained. The mean value, ·60, is higher than ·583 which has been obtained by Stucker * from a series of experiments. It must be remembered, however, that the thickness of the walls of the glass tube used in the present work was of the order of 2 mm.

Experiments to determine the end correction of an open tube fitted with a flange were made corresponding to a half wave-length of 19·7 cm. The cap with the largest aperture was opened until its diameter was exactly equal to the internal diameter of the tube, the flange was fitted over it and measurements were taken to the outside of the cap. In this instance a value of ·79 times the radius was obtained. Substituting the value of the internal radius of the tube in the formula for flanged caps (viz. end

* N. Stucker, *Akad. Wiss. Wien. Ber.* cxvi. pp. 1, 231 (1907).

correction × radius = 5·5), and correcting for the fact that the end corrections were measured from *inside* the cap, a higher value of ·92 is obtained. Rayleigh's * estimate (assuming a long wave-length) was ·82 for an infinite flange.

A point of interest in connexion with the position of the end of the vibrating rod may be noted here. In different experiments for the same cap the readings of the antinodes were constant although the position of the end of the vibrating rod varied considerably—its most frequent positions being between points distant $n \cdot \lambda/2$ and $(n+1/4) \cdot \lambda/2$ from a node (where n is an integer and λ is the wave-length).

The method described is limited by the accuracy with which the positions of the antinodes can be read, but it has the advantage over the ordinary resonance method of Blaikley † in that the aperture is unobstructed by a tuning-fork. Moreover, having varied the position of the fork with respect to the open end of the tube, W. M. Boehm ‡ (who used Blaikley's method in conjunction with a vibration-galvanometer to measure intensity) has concluded that "A maximum of intensity outside the tube may not indicate that the resonator is nearest to unison with the pitch produced." This is noteworthy as revealing a source of error to which experiments made by this method are liable. Curves are given by Boehm showing the relation between end correction and width of flange, and from them he deduces a mean result equal to ·656 times the internal radius for tubes having a thickness of wall of 3·1 mm.; for tubes having an "infinite" flange the results lie between ·849 and ·909 times this quantity.

Efforts are now being made to increase the accuracy and range of measurements by the use of a hot wire detector in conjunction with a valve oscillator.

* Rayleigh, "On the Theory of Resonance," Scientific Papers, vol. i. p. 33.

† D. J. Blaikley, Phil. Mag. ser. 5, vol. vii. p. 339 (1879).

‡ Phys. Review, xxxi. p. 341 (1910).

LX. *The Magnetic Rotary Dispersion of Methyl and Propyl Alcohols.* *By* D. O. Jones, *M.Sc.*, *and* Prof. E. J. Evans, *D.Sc.*, *Physics Department*, *University College of Swansea* *.

Introduction.

THE magnetic rotations of a large number of substances for sodium light have been examined by Perkin and others, and the magnetic rotary dispersion of several substances has been investigated by several observers, notably by Borel, Siertsema, Landau, Meyer, Lowry, Richardson, and Roberts. Our knowledge of the magnetic rotary dispersion of a large number of substances, especially in the ultra-violet region of the spectrum, is still very incomplete, and the present investigation, which is a continuation of the work carried out by Stephens and Evans †, was undertaken with the intention of measuring accurately the magnetic rotation of methyl and propyl alcohol in the region ·4300 μ to about ·2500 μ. The results could then be examined in relation to Larmor's ‡ theory of magneto-optical rotation and the position of the absorption bands determined. Richardson §, in two very interesting papers, discusses fully the magneto-optical properties of several substances in relation to theory, and the nomenclature used in this paper is the same as the one adopted by him.

An expression for the magnetic rotation of a medium may be obtained from the equation expressing the natural dispersion by making use of a formula deduced by Larmor ‖, namely,

$$\delta = \frac{e}{2mC^2}\lambda\frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where δ is the magnetic rotation, C the velocity of light, n the refractive index, and e/m is the ratio of charge to mass for all the resonators.

If the natural dispersion be given by an equation of the Ketteler-Helmholtz type, viz.,

$$n^2-1=b_0+\frac{b_1}{\lambda^2-\lambda_1{}^2}+\frac{b_2}{\lambda^2-\lambda_2{}^2}+\ldots., \quad . \quad . \quad (2)$$

* Communicated by the Authors.
† Phil. Mag., March 1927, p. 546.
‡ 'Æther and Matter,' Appendix F, p. 352.
§ Phil. Mag. xxxi. pp. 232, 454.
‖ Larmor, *loc. cit.*

it can be shown * that

$$\phi = n\delta\lambda^2 = K_1\left(\frac{\lambda^2}{\lambda^2-\lambda_1^2}\right)^2 + K_2\left(\frac{\lambda^2}{\lambda^2-\lambda_2^2}\right)^2 + \ldots., \quad . \quad (3)$$

where k_1, k_2, etc., are constants and λ_1, λ_2, etc., are wave-lengths corresponding to the free periods of the vibrators.

For substances which are transparent in the visible and infra-red, λ_1 and λ_2 will represent wave-lengths corresponding to ultra-violet free periods, and when a substance possesses only one free period in the ultra-violet, the equation reduces to the form

$$\phi = K_1\left(\frac{\lambda^2}{\lambda^2-\lambda_1^2}\right)^2 . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From the two values of ϕ corresponding to two values of λ it is therefore possible to determine k_1 and λ_1 for that region of the spectrum. If it be found that the experimental results lead to different values of λ_1, depending on the wave-lengths chosen, and if the values change progressively when the chosen wave-lengths are taken in regions of shorter and shorter wave-lengths, it is presumed that the substance has more than one free period. If, however, the values of λ_1 were constant within experimental error, the values of ϕ are given by equation (4).

Experimental Arrangement.

A full account of the experimental arrangement has been previously given †, and consequently it is not essential here to describe the apparatus in detail. The source of light, a nickel-steel spark or a tungsten arc, was placed at the focus of a quartz lens, which formed a part of the polarizing unit. The parallel beam of light thus obtained was passed through a Jellet prism, which formed the other part of the polarizing unit, and produced a beam the two semi-circular halves of which were polarized at a small angle with each other. The emergent beam traversed the liquid contained in a polarimeter tube, which is made of clear fused quartz, and is supported by two cork disks inside the core of a solenoid through which a current of 2 amperes was passed. A water-jacket separated the tube from the coil carrying the current, and the temperature of the liquid in the polarimeter tube was kept constant, during an experiment, by

* Richardson, *loc. cit.*

† Stephens & Evans, *loc. cit.*

passing a stream of water through the jacket. On emerging from the polarimeter tube, the beam of light passed through the analyser, and was brought to a focus on the slit of a quartz spectrograph by means of a quartz-fluorite lens.

The polarimeter used in these experiments was supplied by Bellingham and Stanley, and had been designed for work in the ultra-violet region of the spectrum. The two components of the polarizer were assembled without any intervening film, which may cause absorption in the ultra-violet.

The quartz polarimeter tube was 30·5 cm. long and about 1 cm. in diameter, and was closed by fusing on to the ends two disks of polished fused quartz. These disks were fused along the outside circumference of the tube, and in this way the distortion of the beam of light, especially by the central portions of the disks, was avoided. The liquid was introduced through a small neck which had been fused to the middle of the tube, and which was closed by a tight-fitting quartz cap. Owing to the rotation produced by the quartz ends, due to the magnetic field, a correction was necessary in determining the rotation produced by the liquid under investigation. The corrections at definite wave-lengths were determined by special experiments, and the order of the correction can be seen from the result that the measured rotation was 13·4 minutes of arc for the wave-length ·2753 μ.

The solenoid, which was wound on a brass tube 47·3 cm. long and 4·27 cm. diameter, was connected in series with a battery of accumulators, a Weston ammeter, and two variable resistances. One of these resistances was fitted with a fine adjustment, and by means of the Weston ammeter the current of 2 amperes passing through the solenoid could be kept constant to within 1 part in 600. By passing a stream of water through the jacket, and continuously adjusting its rate of flow, the variation in the temperature of the liquid during an exposure could be kept very small. During long exposures of over one hour, the temperature could be kept constant to within 0°·3 C., and in a large number of cases the temperature was constant to within 0°·1 C.

The value of the magnetic field at various points inside the solenoid had been previously determined by Stephens and Evans* by means of a delicate ballistic galvanometer and an accurately constructed search-coil. The value of ΣHl, where H is the magnetic field at a given point of the polarimeter

* *Loc. cit.*

tube and l the length of tube over which H is very approximately constant, was found to be 12445 gauss cm. for the quartz tube employed in the present experiments. The observed and calculated values of the field agreed to within 1 part in 300. An error in the determination of the magnetic field will not affect the relative values of Verdet's constant for different wave-lengths, and it is important to note that the position of the absorption bands can be determined from these relative values.

The spectrograph was constructed in the laboratory, and its optical parts consisted of two quartz lenses and a Cornu quartz prism. Photographs were taken with Imperial and Wellington rapid plates, and exposures with the nickel-steel spark varied from about 45 minutes to 2 hours. The exposures required with the tungsten arc were of smaller duration, but even with the arc, when investigating the region below ·3000 μ for propyl alcohol, exposures of about one hour's duration were necessary. In the case of methyl alcohol, rotations were measured for wave-lengths ranging from ·4400 μ to ·2600 μ, and in the case of propyl alcohol for wave-lengths ranging from ·4400 μ to ·2850 μ.

Mode of Experiment.

The two semi-circular half-fields, consisting of two beams of plane polarized light vibrating in directions making a small angle with each other, after passing through the Cornu prism, gave rise to two spectra, one above the other. These spectra are, in general, of different intensity, but if there is no liquid in the tube, and the magnetic field is absent, it is possible, by rotating the analyser, to make the two contiguous spectra have the same intensity throughout their length. There are four positions of the analyser separated by 90°, which will give equality of fields, and two of these positions, separated by 180°, give a minimum intensity. The position of minimum intensity gives the maximum sensitivity, and the reading on the scale corresponding to this position is called the zero reading of the instrument. When making observations the following procedure was adopted. The polarimeter tube was filled with the liquid and placed inside the solenoid through which a constant current of 2 amperes was passed. The analyser was then rotated through a known angle and the photographic plate exposed. On examining the plate it was seen that the intensities of corresponding lines in the upper and lower spectra were, in general, unequal, but it was possible to determine the wave-length of a definite

line which was of the same intensity in both spectra. It sometimes occurred that this point of equality fell into the small gap between two lines, and in such a case the reading of the analyser was slightly altered, so that the point of equality fell on one of the lines situated on either side of the gap.

Let λ be the wave-length of the line which gave equality of intensity in both spectra, and θ_1 be the corresponding reading of the analyser when the liquid was in the polarimeter tube.

Let θ_2 be the reading of the analyser, which gave equality at the same wave-length with no liquid in the tube, for the same value of the magnetic field.

Then $\theta_1-\theta_2$ gives the rotation corresponding to the wave-length λ produced by the liquid due to a value of ΣHl equal to 12,445 gauss cm. Verdet's constant δ for a given wave-length λ is given by the relation

$$(\theta_1-\theta_2)_\lambda=\delta_\lambda \Sigma Hl,$$

and can therefore be determined for the various wave-lengths. The same values of δ_λ were obtained when the magnetic field was reversed and the analyser was rotated through the same angles in the opposite direction.

The rotation corresponding to a particular wave-length was repeated several times, and it is considered that the absolute values of Verdet's constant are correct to about $\frac{1}{3}$ per cent. on the average.

Experimental Results.

Methyl Alcohol.

The magnetic rotation of methyl alcohol for sodium light has been determined by Quincke *, who obtained the value ·00989 for Verdet's constant. The molecular magnetic rotation relative to water was determined for the same wave-length by Perkin †, who obtained the value 1·640 at 18°·7 C. The value of Verdet's constant for methyl alcohol calculated from Perkin's result is ·00956 at 18°·7 C. The rotation of methyl alcohol for ·4359 μ relative to the rotation for ·5461 μ was determined by Lowry ‡, who found the value 1·629. In the present experiments the magnetic rotations of pure methyl alcohol were determined for about fifteen wave-lengths ranging from ·4380 μ to about ·2600 μ,

* *Wied. Ann.* xxiv. p. 614 (1885); Landolt & Börnstein, ii. p. 1013.
† Journ. Chem. Soc. xlv. p. 466 (1884).
‡ Journ. Chem. Soc. l. p. 91 (1914).

and the values of Verdet's constant were determined for those wave-lengths. Two series of experiments were carried out with the alcohol, and the results are given in Tables I. (*a*) and I. (*b*). The density of the methyl alcohol at 15° C. and its boiling point were determined and found to be ·797 and 64°·7 C. respectively.

Table I. (*a*).

Temperature in degrees centigrade.	Wave-length in microns (10^{-4} cm.).	Verdet's Constant in min. per cm. gauss.	Refractive Index, *n*.
7·8	·4380	$\cdot 0181_9$	1·3365
7·6	·4360	$\cdot 0184_2$	1·3366
8·5	·4260	$\cdot 0193_6$	1·3371
8·5	·4045	$\cdot 0217_3$	1·3387
8·4	·3828	$\cdot 0246_6$	1·3405
8·3	·3600	·0286	1·3435
8·3	·3404	$\cdot 0326_2$	1·3462
8·1	·3175	$\cdot 0386_3$	1·3504
8·0	·3155	·0395	1·3508
8·2	·2980	$\cdot 0455_8$	1·3547
8·3	·2967	·0464	1·3550
8·2	·2925	·0473	1·3562
8·1	·2850	$\cdot 0508_8$	1·3583
8·2	·2756	$\cdot 0560_4$	1·3617

Table I. (*b*).

Temperature in degrees centigrade.	Wave-length in microns (10^{-4} cm.).	Verdet's Constant in min. per cm. gauss.	Refractive Index, *n*.
8·7	·4378	$\cdot 0181_9$	1·3365
9·2	·4256	$\cdot 0193_6$	1·3371
8·7	·4055	$\cdot 0217_3$	1·3386
9·3	·3958	·0229	1·3394
8·5	·3826	$\cdot 0246_6$	1·3406
9·7	·3595	$\cdot 0286_6$	1·3435
9·3	·3413	.0326	1·3460
9·0	·3200	$\cdot 0381_4$	1·3498
8·7	·2855	$\cdot 0508_8$	1·3582
8·9	·2757	$\cdot 0560_4$	1·3618

The methyl alcohol was then introduced into a flask fitted with fractionating column and distilled. The middle fraction was retained, and employed in the determination of Verdet's

constant for several wave-lengths. The results obtained with the distilled liquid were practically the same as those previously obtained with the unfractionated liquid, and are given in Table II. There was evidence, however, that the original material contained a very small trace of a substance absorbing light between ·2700 μ and ·2600 μ. Experiments on the rotation have been carried out with the liquid subjected to further fractional distillation, but the results were exactly the same as before.

Table II.

Temperature in degrees centigrade.	Wave-length in microns (10^{-4} cm.).	Verdet's Constant in min. per cm. gauss.	Refractive Index, n.
8·7	·4380	$·0181_9$	1·3365
9·2	·4050	$·0217_3$	1·3386
9·0	·3602	·0286	1·3435
9·3	·3196	$·0381_4$	1·3498
8·5	·3108	$·0404_5$	1·3517
8·8	·2980	$·0455_3$	1·3547
8·8	·2856	$·0508_8$	1·3583
9·6	·2754	$·0560_4$	1·3618
9·5	·2627	$·0637_2$	1·3672

In the last column of Table III. are calculated the values of the function ϕ (which is equal to $n\delta\lambda^2$) for different wave-lengths. The values of the refractive indices of methyl alcohol have been obtained from a graph, which has been constructed from values given by Victor Henri *.

Table III.

Wave-lengths in microns.	Refractive Index, n.	Verdet's Constant in min. per cm. gauss.	Verdet's Constant in circular measure, $\times 10^6$, *i. e.*, $\delta\times10^6$.	$\phi\times10^{14}$ ($\phi=n\delta\lambda^2$).
(*a*) ·4379	1·3365	$·0181_9$	5·291	1·356
(*b*) ·4050	1·3387	$·0217_3$	6·321	1·388
(*c*) ·3600	1·3435	·0286	8·319	1·449
(*d*) ·3198	1·3498	$·0381_4$	11·094	1·532
(*e*) ·2980	1·3547	$·0455_3$	13·259	1·595
(*f*) ·2754	1·3618	$·0560_4$	16·301	1·684
(*g*) ·2628	1·3667	$·0637_2$	18·535	1·750

* 'Etudes de Photochemie,' p. 61.

We have not been able to find a reference to the temperature at which the determinations of refractive indices have been carried out, but by comparison with values given in Landolt and Börnstein *, it is presumed that the temperature was in the neighbourhood of 17° C. Also the values given in Landolt and Börnstein † for the refractive indices of methyl alcohol at 15°·5 C. in the ultra-violet agree for wave-lengths above ·2900 μ to about 1 in a 1000 with the values given in Tables I. and II., but the values for wave-lengths in the neighbourhood of ·2700 μ differ by about 1 in 400 from those given in the Tables. The experiments on magnetic rotation were carried out at temperatures in the neighbourhood of 8° C., and, owing to a small negative temperature coefficient, the refractive indices corresponding to 8° C. will probably be slightly higher than the values given in Tables I. and II. The values of λ_1 (the wave-length of the absorption band) will not, however, be seriously affected by the small corrections to be applied to the refractive indices, as λ_1 is calculated from the ratio of two values of $\phi(n\delta\lambda^2)$ corresponding to two wave-lengths.

The values of λ_1, the wave-length of the absorption band determined from the above observations on the assumption that

$$\phi = K_1\left(\frac{\lambda^2}{\lambda^2-\lambda_1{}^2}\right)^2,$$

are as follows :—

From (a) and (b) = ·1108 μ.	From (a) and (d) = ·1101 μ.
„ (b) and (c) = ·1100 μ.	„ (a) and (g) = ·1100 μ
„ (c) and (d) = ·1099 μ.	„ (d) and (g) = ·1099 μ.
„ (d) and (e) = ·1094 μ.	„ (b) and (e) = ·1098 μ.
„ (e) and (f) = ·1096 μ.	„ (e) and (g) = ·1101 μ.
„ (f) and (g) = ·1108 μ.	„ (c) and (f) = ·1095 μ.

The mean value of λ_1 is approximately ·1100 μ, and the magnitude of K_1 in the above formula can be calculated from the value of ϕ corresponding to a known value of λ. The calculated value of K_1 is 1·190, and the variation of ϕ with wave-length in the visible and ultra-violet regions of the spectrum is given by the equation

$$\phi = 1{\cdot}190\left(\frac{\lambda^2}{\lambda^2-(\cdot 1100)^2}\right)^2.$$

* Vol. ii. p. 968.
† *Loc. cit.*

A further test of the accuracy of the above equation is obtained by calculating the values of ϕ and hence δ corresponding to different wave-lengths in the visible and ultra-violet regions of the spectrum, and comparing the calculated values of Verdet's constant with those obtained experimentally. The results of the calculations are given in Table IV.

TABLE IV.

Wave-length in microns.	Verdet's Constant calculated.	Verdet's Constant observed.
·5893	·00951	·00956 *
·4258	·0193$_6$	·0193$_6$
·3958	·0228$_8$	·0229$_0$
·3826	·0247$_6$	·0246$_3$
·3413	·0326	·0324$_7$
·3108	·0408	·0405
·2855	·0509$_2$	·0508$_8$

* Calculated from Perkin's result.

The Magnetic Rotary Dispersion of Normal Propyl Alcohol.

The magnetic rotation of propyl alcohol relative to water for sodium light was determined by Perkin *, who found the value ·9139 at 15°·6 C. The value of Verdet's Constant calculated from the above result is ·01197. The value of the rotation at ·4359 μ relative to its value at ·5461 μ has been determined by Lowry †, who found 1·635 for $\frac{\delta_{\cdot 4359\,\mu}}{\delta_{\cdot 5461\,\mu}}$.

In the present experiments the rotation of propyl alcohol for several wave-lengths ranging from ·4400 μ to ·2850 μ has been measured, and the results have been collected in Tables V. to IX. Several samples of normal propyl alcohol were employed, but in all cases it was found that they contained a small quantity of an active impurity producing a natural rotation, which was superimposed on the rotation produced by the magnetic field. In the present experiments, for the direction of the magnetic field mainly employed, the natural rotation was in the opposite direction to that produced by the field.

Normal propyl alcohol is generally prepared by the

* Journ. Chem. Soc. xlv. p. 467 (1884).
† *Ibid.* l. p. 91 (1914).

fractional distillation of fusel oil, which contains normal amyl alcohol and other homologues of the alcohol series. It is therefore suggested that the optically active impurity is lævo-rotary amyl alcohol, which boils at 128° C. In one of the earlier samples experimented upon, this natural rotation amounted to 49·3 minutes at ·3420 μ. Under these circumstances the total rotation produced by the propyl alcohol when placed in a magnetic field is equal to the magnetic rotation due to the normal propyl alcohol plus the sum of the natural and magnetic rotations due to the impurity. It has been assumed in constructing Tables V., VI. and VII. that the magnetic rotation of pure normal propyl alcohol for a given λ is equal to the sum of the measured rotation in the magnetic field and the natural rotation for that wave-length. It is considered that, as the quantity of impurity is comparatively small, and as it is probably active amyl alcohol whose strong absorbtion band is near that of propyl alcohol, the error introduced by the above mode of calculation is very small. The magnetic rotation of the propyl alcohol was also measured for two wave-lengths when the magnetic field was reversed, and the magnetic rotation was in the same direction as the natural rotation due to the impurity. The values of the magnetic rotation were found to be the same as before.

The results given in Tables V. to IX. refer to the purest normal propyl alcohol prepared by Dr. Schuchardt of Görlitz. The liquid was placed in a flask provided with a fractionating column, and practically all of it distilled over at a constant temperature of 97° C. The alcohol was also satisfactory from the point of view of absorption in the ultra-violet. With the tungsten arc as the source of light, magnetic rotations could be measured for wave-lengths in the ultra-violet as far as ·2800 μ. The alcohol, however, showed the presence of a small quantity of impurity which was optically active. The results of experiments on what is called the first sample of normal propyl alcohol are given in Table V. In this sample the natural rotation, which was measured for several wave-lengths, varied from 12 min. at ·4500 μ to 33·1 min. at ·2850 μ. The propyl alcohol was then purified by repeated fractional distillation, and the results for the second sample are given in Table VI.

The natural rotations for this sample were also measured at different wave-lengths, and were found to vary from 4·7 min. at ·4500 μ to 13·9 min. at ·2850 μ.

The alcohol was again purified by fractional distillation over a long period, and the results for the third sample are given in Table VII. The natural rotation for this sample varied from 2·7 min. at ·4500 μ to 7·7 min. at ·2850 μ.

In this case the natural rotation for sodium light would be about 1·46 min. The rotation for sodium light found by Pedler * for the purest lævo-rotary amyl alcohol he could obtain was $-6^{\circ}\cdot8$ for 200 mm., and consequently, if the tube used in the present experiments contained pure optically active amyl alcohol, the rotation could not be less than 622 min. The percentage of optically active substance contained in the third sample, if it be assumed that the impurity is active amyl alcohol, is, therefore, not greater than ·23 per cent., and the correction to be applied for the natural rotation is only about 1 per cent. of the magnetic rotation. The results obtained, as explained above, for the samples containing various percentages of the active impurity are in good agreement. In these experiments the presence of the active impurity is easily detected, especially in the ultra-violet, owing to the length of tube employed, but the results obtained seem to indicate that

TABLE V.

First Sample of Propyl Alcohol.

Temperature in degrees centigrade.	Wave-length in microns (10^{-4} cm.),	Verdet's Constant in min. per cm. gauss.	Refractive Index, n.
17·0	·4390	$\cdot0227_7$	1·3935
16·5	·4300	·0240	1·3942
16·8	·4055	$\cdot0273_5$	1·3973
17·0	·3975	·0287	1·3983
15·5	·3894	$\cdot0301_5$	1·3993
15·0	·3670	$\cdot0346_5$	1·4025
17·0	·3600	$\cdot0362_8$	1·4034
15·5	·3406	·0417	1·4069
16·5	·3306	$\cdot0445_5$	1·4094
16·0	·3180	$\cdot0492_2$	1·4119
16·7	·3115	·0520	1·4140
16·9	·3055	$\cdot0541_5$	1·4152
17·0	·2960	·0594	1·4182
16·9	·2940	$\cdot0602_6$	1·4188
16·4	·2856	·0647	1·4216

* Perkin, *loc. cit.*

Table VI.

Second Sample of Propyl Alcohol.

Temperature in degrees centigrade.	Wave-length in microns (10^{-4} cm.).	Verdet's Constant in min. per cm. gauss.	Refractive Index. n.
16·7	·4310	·0239	1·3941
16·0	·3975	$\cdot 0286_6$	1·3983
16·6	·3895	·0301	1·3992
16·5	·3675	·0346	1·4023
15·1	·3400	$\cdot 0415_8$	1·4070
15·6	·3203	$\cdot 0482_5$	1·4114
16·2	·3065	$\cdot 0540_5$	1·4150
16·8	·2945	·0603	1·4187
17·1	·2850	·0650	1·4219

Table VII.

Third Sample of Propyl Alcohol.

Temperature in degrees centigrade.	Wave-length in microns (10^{-4} cm.).	Verdet's Constant in min. per cm. gauss.	Refractive Index, n.
17·2	·4295	·0240	1·3943
17·8	·3985	·0285	1·3982
17·7	·3910	·0299	1·3991
17·6	·3670	·0346	1·4025
17·5	·3399	·0416	1·4070
17·5	·3205	·0482	1·4114
17·2	·3060	·0542	1·4150
17·5	·2936	·0604	1·4189

Table VIII.

Wave-length in microns (10^{-4} cm.).	Refractive index, n.	Verdet's Constant in min. per cm. gauss.	Verdet's Constant in circular measure, $\times 10^6$, *i. e.*, $\delta \times 10^6$.	$\phi \times 10^{14}$ ($\phi = n\delta\lambda^2$).
(a) ·4295	1·3943	·0240	6·981	1·796
(b) ·3985	1·3982	·0285	8·290	1·841
(c) ·3670	1·4025	·0346	10·065	1 901
(d) ·3205	1·4114	·0482	14·021	2·033
(e) ·2936	1·4189	·0604	17·570	2·149

practically no improvement would be obtained by further fractional distillation. The values of the refractive indices given in Tables V., VI., VII., and VIII. have been obtained from a graph, which has been constructed from values given by Victor Henri*. In this case again we have been unable to find a reference to the temperature at which the measurements were made, but values of the refractive indices of normal propyl alcohol at 18° C. in the ultra-violet† differ by about 1 in 400 from the values given in the Tables VI. to VIII. for wave-lengths between ·2800 and ·3080 μ, and by about 1 in 1000 for wave-lengths between ·3080 and ·3940 μ.

The values of the function from which the wave-length λ_1 of the absorption band is calculated are given in Table VIII.

The values of λ_1, the wave-length of the absorption band determined from the above observations on the assumption that

$$\phi = K_1\left(\frac{\lambda^2}{\lambda^2-\lambda_1{}^2}\right)^2,$$

are as follows :—

From (*a*) and (*b*) = ·1143 μ.
„ (*b*) and (*c*) = ·1142 μ.
„ (*c*) and (*d*) = ·1134 μ.
„ (*d*) and (*e*) = ·1134 μ.
From (*a*) and (*c*) = ·1143 μ.
„ (*c*) and (*e*) = ·1134 μ.
„ (*a*) and (*e*) = ·1137 μ.

The mean value of λ_1 is ·1138 μ, and the value of K_1 calculated from the value of ϕ corresponding to a known value of λ was found to be 1·553. The variation of ϕ with wave-length in the visible and ultra-violet regions of the spectrum is therefore given by the equation

$$\phi = 1{\cdot}553\left(\frac{\lambda^2}{\lambda^2-(\cdot 1138)^2}\right)^2.$$

A further test of the accuracy of the above formula is obtained by making use of it to calculate the values of Verdet's constant for different wave-lengths in the visible and ultra-violet regions of the spectrum, and comparing the results obtained with those determined experimentally. Table IX. gives the results of such calculations.

* V. Henri, *loc. cit.*
† Landolt & Börnstein, ii. p. 969.

Table IX.

Wave-length in microns (10^{-4} cm.).	Verdet's Constant observed.	Verdet's Constant calculated.
·4390	$\cdot 0227_7$	·0228
·4055	$\cdot 0273_5$	$\cdot 0273_7$
·3910	·0299	·0298
·3895	·0301	$\cdot 0300_7$
·3600	$\cdot 0362_8$	$\cdot 0362_4$
·3399	·0416	$\cdot 0416_3$
·3306	$\cdot 0445_5$	·0446
·3180	$\cdot 0492_2$	·0492
·3115	·0520	·0518
·3060	·0542	$\cdot 0542_6$
·2960	·0594	·0592
·2856	·0647	·0650

If the equation be employed to determine the value of Verdet's constant for sodium light, the result obtained is $\cdot 0119_6$. This calculated value is in good agreement with that determined experimentally by Perkin *, viz., ·01197.

Discussion of Results.

The experimental results obtained for methyl alcohol over the range ·4379 μ to about ·2600 μ can be represented by the equation

$$n\delta\lambda^2 = \phi = 1\cdot 190\left(\frac{\lambda^2}{\lambda^2 - (\cdot 1100)^2}\right)^2,$$

where δ = Verdet's constant, n the refractive index of the liquid for wave-length λ, and ·1100 μ is the wave-length corresponding to the free period of the resonators.

The corresponding expressions for ethyl alcohol over the range ·4390 μ to ·2600 μ, and for propyl alcohol over the range ·4390 μ to ·2856 μ, are

$$n\dagger\delta\lambda^2 = \phi = 1\cdot 444\left(\frac{\lambda^2}{\lambda^2 - (\cdot 1114)^2}\right)^2$$

* *Loc. cit.*

† Stephens & Evans, *loc. cit.*

and

$$n\delta\lambda^2 = \phi = 1{\cdot}553\left(\frac{\lambda^2}{\lambda^2-(\cdot 1138)^2}\right)\ldots$$

respectively.

The magnetic rotations over the ranges of spectrum investigated can therefore in each case be represented by a formula involving only one free period, and also the values of Verdet's constant for sodium light deduced from the three equations agree, within the limits of experimental error, with those determined by Perkin * for the three alcohols. It is also evident from the three equations that the absorption band shifts towards the region of longer wave-length as the molecular weight of the alcohol increases but the change in the frequency of the absorption band in passing from one alcohol to the next in the series does not appear to be constant.

The dispersion and absorption of the alcohols in the ultra-violet and infra-red regions of the spectrum have been measured by Victor Henri †. From these data he concluded that the alcohols have absorption bands of frequencies related to one another, as follows:—

$\underbrace{\frac{\nu_0}{4}, \frac{\nu_0}{2}, \nu_0, 2\nu_0,}$	$15\nu_0,$	$30\nu_0,$
infra-red;	ultra-violet;	extreme ultra-violet.

From his experimental results on the absorption of light by methyl, ethyl, and propyl alcohols he obtained for the wave-lengths of the absorption bands in the central region of the ultra-violet (corresponding to $15\nu_0$) the values ·2207 μ, ·2231 μ, and ·2273 μ respectively.

It is interesting to point out that the wave-lengths of the absorption bands deduced in the present investigation from measurements of the magnetic rotation of methyl, ethyl, and propyl alcohols are ·1100 μ, ·1114 μ, and ·1138 μ respectively.

The frequencies of these bands are very approximately double the frequencies determined by Victor Henri ‡ in the central region of the ultra-violet, and correspond to $30\nu_0$ in the above scheme. The bands at ·2207 μ, ·2231 μ, and ·2273 μ do not contribute materially to the magnetic rotation of methyl, ethyl, and propyl alcohols respectively.

* *Loc. cit.*

† 'Etudes de Photochemie,' pp. 41–64.

‡ *Loc. cit.*

From the equations for ϕ in the case of methyl and propyl alcohols the values of $\frac{\delta_{\cdot 4359\,\mu}}{\delta_{\cdot 5461\,\mu}}$ were calculated, and found to to be 1·640 and $1{\cdot}645_6$ respectively.

These values are about ·6 per cent. higher than those determined experimentally by Lowry *.

Summary of Results.

1. The magnetic rotation of methyl alcohol has been examined for wave-lengths ranging from ·4379 μ to ·2600 μ, and the values of δ (Verdet's constant) can be represented by the equation

$$\phi = n\delta\lambda^2 = 1{\cdot}189\left(\frac{\lambda^2}{\lambda^2-(\cdot 1100)^2}\right)^2,$$

where n is the refractive index of methyl alcohol for wave-length λ and ·1100 μ is the wave-length of absorption band in the extreme ultra-violet.

The weak absorption band in the central region of the ultra-violet at ·2207 μ does not contribute materially to the magnetic rotation, but the wave-length of the strong absorption band (·1100 μ) deduced from the magnetic rotation experiments is very nearly one half that of the weak absorption band.

2. The magnetic rotation of propyl alcohol has been examined over the range ·4390 μ to ·2856 μ, and the value of δ can be represented by the equation

$$\phi = n\delta\lambda^2 = 1{\cdot}553\left(\frac{\lambda^2}{\lambda^2-(\cdot 1138)^2}\right)^2.$$

The wave-length of the absorption band (·1138 μ) is almost exactly one half that of the weak absorption band at ·2273 μ, but the latter does not contribute materially to the magnetic rotation.

The authors wish to thank Mr. C. C. Evans, B.Sc., for his help during the later stages of the investigation, and also Mr. Frank Homeyard, who was responsible for making most of the apparatus employed in the research.

* *Loc. cit.*

LXI. *On the Properties of Dry Liquids.*

By Prof. S. B. Mali, *D.Sc., A.E.S.* *

PROF. BAKER has recently shown that the boiling-points of many liquids which are ordinarily supposed to be pure are markedly changed when these liquids are subjected to intensive desiccation for a long time (J. C. S. vol. ci. p. 2329, 1912). He proved experimentally that the change in the boiling-points of the liquids had really been brought about by the removal of water, for the introduction of the slightest amount of moisture restored the boiling-points to their former values. He also satisfied himself that the effect was not due to the superheating of the liquids.

As an explanation of this phenomenon, Baker suggested that in the liquid state there is ordinarily a balance between associated and dissociated molecules, and that the absence of water-vapour tends to prevent the dissociation, so that the boiling-points of dried liquids consisting mostly of associated molecules is much higher than for normal liquids.

In 1922, Dr. A. Smits explained Baker's results by supposing that "by intensive drying the inner transformations in a unary phase are stopped, the inner equilibrium is fixed, and a mixture is obtained which on distillation generally gives a distillate with a lower boiling-point and a residue with a higher boiling-point than the original liquid" (*Zeits. Phys. Chem.* c. p. 477, 1922).

In 1923, Prof. G. N. Lewis contradicted, on thermodynamic grounds, the explanations put forward by Smits (J. A. C. S. xlv. p. 2836, 1923). According to him, the mere removal of the last traces of water from a liquid cannot appreciably change the existing equilibrium between several molecular species which may be supposed to exist; but if water acts as a catalyst for the process of interchange between one molecular species and another, its removal can only serve to freeze the already existing state of equilibrium by inhibiting further interchange among the various forms.

In response to these objections, Smits modified his views later. He assumed that in ordinary liquids there are at least two modifications with different properties between which reversible reactions of the type $\alpha \rightleftarrows \beta$ are always taking place. By the process of drying, the velocity of one or both of these reactions is attenuated or even reduced to zero.

* Communicated by the Author.

If the velocity of only one of these reactions (say $\alpha \rightarrow \beta$) is attenuated, we shall have in the dried liquid a mixture of α and β, the quantity of α predominating over that of β. The effect of drying in this case will be a shift of the inner equilibrium followed by freezing or fixation of the inner equilibrium. If, on the other hand, the velocities of both these reactions ($\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$) are attenuated, we shall have in the dried liquid a mixture of the two compounds α and β, in the same proportions in which they exist in moist liquids and between which there may be further mutual transformations. The effect of drying in this case will be simply the fixation of the inner equilibrium. If water acts as a catalyst for one reaction, the vapour-pressure (and hence the boiling-point) of the dried liquid will change, independent of whether or not the distillate is allowed to escape. On the other hand, if water acts as a catalyst for the direct as well as the reverse reactions between the components α and β, the boiling-point of the dried liquid will change only when the distillate is allowed to escape, and not otherwise. Hence, Smits suggests that, if the vapour-pressure (and hence the boiling-point) of the dried liquid changes without any portion of the liquid boiling off, it must be due to shift of the inner equilibrium followed by fixation ; if not, the effect must be simply due to a fixation of the inner equilibrium.

The present writer tested the suggestions of Smits experimentally, and he found that in the case of dried liquids the inner equilibrium is first shifted and then fixed (*Zeitschr. f. Anorg. u. Allg. Chemie*, cxlix. p. 150, 1925).

It appears that the physical properties of ordinary liquids (*e. g.* density, refractive index, viscosity, surface-tension, and conductivity) are but the properties of mixtures. The properties of the components of ordinary liquids which are supposed to be binary mixtures may be studied by drying the liquids intensively so that in the dried product only one component prevails. Since by intensive drying the nature and the relative amount of the molecules in a liquid are changed, it is expected that the absorption spectra of dried liquids and their vapours will differ from the absorption spectra of moist liquids and their vapours; and on account of the predominance in the dried liquids of one kind of molecule over the other, the absorption bands and lines will differ in intensity in the case of moist and dry liquids and their vapours.

No attempts seem to have as yet been made to calculate the relative amounts of the two components in moist and dried liquids which are supposed to be binary mixtures.

The following is an attempt in this direction in the case of those liquids whose rise of boiling-point by drying was measured by Baker. A binary moist liquid will contain the two components α and β in a certain fixed proportion. By drying, this proportion will change, the relative amount of the less volatile component increasing. We may suppose that the dried liquid is for all practical purposes a solution of a portion of the less volatile component in a mixture of the two components existing in the same proportion in which they exist in a moist liquid. Of course in the dried liquid we have actually a solution of the less volatile component in the more volatile component, but, for want of data, we make the above simplifying assumptions in order to render the calculation possible. Suppose in the moist liquid we have the two components α and β in the percentage proportion $x : 100-x$, and suppose that in the dried liquid the percentage is changed to $x' : 100-x'$. If $x' < x$, we may suppose that the dried liquid is a solution of β in a mixture of α and β, and that an amount

$$\left\{(100-x')-\frac{(100-x)x'}{x}\right\}$$

of the solute β is contained in an amount

$$\left\{x+\frac{(100-x)x'}{x}\right\}$$

of the solution.

We know from thermodynamics that there is a relation between the rise of the boiling-point of the solution and the amount of solute present in the solution. For a dilute solution the relation is given by the formula

$$M=\frac{RT_0^2x}{VL\rho\Delta T}$$

or

$$\frac{x}{M}=\frac{VL\rho\Delta T}{RT_0^2},$$

where M = molecular weight of the solute,

x = grams of solute disolved in V c.c. of the solution,

T_0 = absolute boiling-point of the solvent,

L = latent heat of evaporation of one gram of the solvent,

ρ = density of the solvent in grams per c.c.

ΔT = rise of boiling-point of the solution, and

R = gas constant for a gram mol.

If we consider the molar amount of the solute dissolved in 1 c.c. of the solution, the formula may be simplified to the form

$$\frac{x}{M} = \frac{L\rho\Delta T}{RT_0^2}.$$

In the case of a concentrated solution a correction to this formula has to be applied on account of the volume of the solute molecules. If the volume correction for a gram mol. of the solute be "b," the molar concentration of the solute will be given by the formula

$$\frac{\frac{x}{M}}{1-b\frac{x}{M}} = \frac{L\rho\Delta T}{RT_0^2}.$$

The value of "b" being unknown, the calculated values of

$$\frac{\frac{x}{M}}{1-b\frac{x}{M}}$$

corresponding to the liquids intensively dried by Prof. Baker are given in the following table (p. 613). The values of ΔT are taken from Baker's paper (Trans. Chem. Soc. cxxi. p. 568, 1922). The values of the other quantities are taken from Kaye and Laby's 'Tables of Physical Constants.' It may be remarked here that Baker found that the densities of dry liquids do not appreciably differ from the densities of moist liquids.

The values in the last column are calculated on the assumption that the molecules are normal and not associated. If association be supposed to exist, these values will be lowered. The true concentrations of the solutes will be lower than those given in column 6 in the ratio $\left(1-b\frac{x}{M}\right):1$.

A glance at columns 6 and 7 will show that in the case of benzene, CS_2, CCl_4, and bromine the amount of the less volatile component in the dried liquid is very large compared with the amount of the more volatile component. In the case of ethyl alcohol, methyl alcohol, propyl alcohol, and ethyl ether the total number of mols of solute in 1 c.c. of the solution (dried liquid) is much greater than the total number of mols of the solvent in 1 c.c. of the moist liquid, unless

the values of "b" be supposed to be excessively large. If we suppose that the value of "b" is of the same order in the case of all the solutions, we cannot explain the anomalies in the case of the alcohols and ether without supposing that in the dried liquid the molecules are dissociated—a fact which will be in direct contradiction to the explanation put forward by Prof. Baker himself. It thus appears that in the case of alcohols and ether the molecular volumes of the less volatile components are excessively large compared with the molecular volumes of the more volatile components.

Name of liquid.	Density in grams per c.c.	Boiling-point in ° C.	Latent heat of evaporation for 1 gram.	ΔT.	$\frac{\frac{x}{\bar{M}}}{1-b\frac{x}{\bar{M}}}=\frac{L_\rho \Delta T}{RT_0}$.	Gram mol. of moist liquid in 1 c.c. (molecules supposed to be normal.)
Benzene.	$\frac{0{\cdot}879}{20°\,C.}$	80·2	95·49	26	0·009	0·011
CS_2.	$\frac{1{\cdot}292}{0°\,C.}$	46·2	85	30	0·016	0·017
CCl_4.	$\frac{1{\cdot}582}{21°\,C.}$	76·7	46	34	0·010	0·010
Ethyl alcohol.	$\frac{0{\cdot}7937}{15°\,C.}$	78·3	207	60	0·04	0·017
Methyl alcohol.	$\frac{0{\cdot}796}{15°\,C.}$	64·7	267	54	0·050	0·025
Bromine.	$\frac{3{\cdot}102}{25°\,C.}$	63	46	55	0·0348	0·0388
Mercury.	$\frac{1\,56}{15°\,C.}$	356·7	68	62	0·072	0·067
Ethyl ether.	$\frac{0{\cdot}718}{17°\,C.}$	34·6	84	48	0·0152	0·097
Propyl alcohol.	$\frac{0{\cdot}804}{20°\,C.}$	97·2	163	39	0·019	0·0133

The catalytic behaviour of water in the transformations of the components of binary mixtures of moist liquids may be explained on Baly's theory of residual affinity (Baly's 'Spectroscopy,' 1918 ed., p. 487). Under residual affinity Baly includes every type of unsaturation whether as regards the primary or the secondary valencies. Since the possession of residual affinity tends to endow a compound with the

power of forming additional compounds with other substances, the existence of residual affinity is accompanied by the existence of force lines in the surrounding æther. Every group of atoms must have round it a field of force whose magnitude must depend on the amount of residual affinity present. As a consequence, there must be a certain amount of condensation of the lines of force of the various atom groups, and the system will be more or less closed. If these closed systems receive suitable energies they may open again. The presence of a third substance may serve to open these compounds so that they will be capable of free existence and also will be free to take part in chemical reactions. This third substance can open the compounds by itself absorbing radiations selectively (probably in an excited state) and emitting them again in the space occupied by the compounds. It thus plays the role of a catalytic agent.

Coming now to the problem in hand, we may suppose that the simple unassociated molecules of a dry liquid do ordinarily form compounds among themselves on account of their residual affinities. But in the presence of moisture these molecules are energized by radiations selectively absorbed and radiated by water molecules, and are capable of indepedent existence as individual molecules. The amount of radiation from the water molecules which energizes the closed molecular systems of the moist liquid must be a function of temperature, and it is expected to increase with temperature. On this theory we expect that at very low temperatures most of the molecules of a moist liquid will behave as closed systems. In other words, there will be little or no difference between a moist and a dry liquid at very low temperatures according to the present theory.

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Note added in proof.—In the case of nitrogen tetroxide Smits (J. C. S., Oct. 1926) proved that the vapour-pressure rises with drying, and this result has recently been corroborated by Smith. It therefore appears that moisture not only retards association in liquids, but sometimes also promotes it. The catalytic behaviour of water in moist liquids therefore appears to be a complex thing. Besides, there is reason to believe that most of the water molecules in moist liquids are in an ionized state, and it is the ions that are responsible for the catalytic behaviour of water.

LXII. *A Modification of the Rayleigh Disk Method for measuring Sound-Intensities.* *By* L. J. Sivian *.

THE usual procedure is to measure the steady deflexion of the disk under the influence of a steady sound-field. Following is an outline of a procedure which has been found useful when the sound amplitude can be made a suitable function of time. The scheme depends on the fact that the torque which the sound-wave exerts on the disk is a non-linear function of the sound amplitude. The amplitude of the sound-wave to be measured is modulated with a frequency equal to that of the free vibration of the suspended disk. The measurement consists in reading the amplitude of oscillations corresponding to the modulating frequency, rather than a steady deflexion of the disk. The disturbances caused by spurious air-currents are largely reduced. In addition, for many practical cases at least, there is a gain in absolute sensitivity.

For a thin circular disk whose normal makes an angle θ with the direction of the undisturbed fluid stream, the torque M tending to diminish θ is † :

$$M = \frac{4}{3}\rho a^3 \cdot U^2 \cdot \sin 2\theta, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ = fluid intensity, a = radius of disk, and U = stream-velocity. If, as in a sinusoidal sound-wave, $U = U_0 \cdot \sin nt$,

$$M = \frac{4}{3}\rho a^3 \cdot \sin 2\theta \cdot \left(\frac{1}{2} - \frac{1}{2}\cos 2nt\right) U_0^2$$

$$= B \cdot \frac{1}{2} U_0^2 - B \cdot \frac{1}{2} U_0^2 \cdot \cos 2nt.$$

The torque contains a rectified and a double-frequency component. The former accounts for the deflexion observed in the static method. The alternating component usually is unobservably small, owing to the high motional impedance of the disk at the sound-frequencies.

Suppose, now, that a completely modulated wave

$$U = U_0 \cdot (1 + \sin \omega t) \cdot \sin nt \quad . \quad . \quad . \quad . \quad (2)$$

is incident upon the disk. The torque acting is

$$M(t) = B \cdot \frac{1}{2} U_0^2 \left[\frac{3}{2} + 2 \sin \omega t - \frac{1}{2}\cos 2\omega t\right](1 - \cos 2nt).$$

* Communicated by Rollo Appleyard, M.Inst.C.E.

† W. König, Wied. *Ann.* xliii. p. 43 (1891).

If the motion of the disk is given by

$$I\ddot{\phi} + R\dot{\phi} + S\phi = M(t),$$

the modulating frequency is chosen so that

$$I\omega^2 - S = 0.$$

If $n >> \omega$, as is the case in practice, the steady state deflexions produced by the modulated torque, which need be considered, are:

$$\left.\begin{aligned} D_0 &= \frac{3}{4} B U_0^2 \cdot \frac{1}{S}, \\ D_1 &= B U_0^2 \cdot \frac{1}{R\omega}, \\ D_2 &= \frac{1}{4} B U_0^2 \cdot \frac{1}{2R\omega \sqrt{1 + \frac{9S^2}{4R^2\omega^2}}}, \end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

where D_0 is a steady deflexion, D_1 corresponds to the frequency $\frac{\omega}{2\pi}$, and D_2 to $\frac{2\omega}{2\pi}$. D_1 is the amplitude observed in the dynamic method. In the static method, $D_s = \frac{3}{4} B U_0^2 \cdot \frac{1}{S}$ for an unmodulated wave of the same r.m.s. amplitude as in the modulated wave assumed above. The ratio $\frac{D_1}{S_s} = \frac{4}{3} \cdot \frac{S}{R\omega}$ gives the relative sensitivity of the two methods. Suppose, further, that the spurious air-drifts produce essentially a steady torque. Then, as a rough approximation, the "sound-drift ratio" is $\frac{4}{3} \cdot \frac{S}{R\omega}$ times greater for the dynamic than for the static method. A numerical example will indicate the orders of magnitudes involved. For a certain disk designed to measure D_s, T = period = 2·59 sec., $R = 3{\cdot}53 \times 10^{-5}$, and $I = 8{\cdot}04 \times 10^{-5}$. The value of $\frac{4}{3} \cdot \frac{S}{R\omega}$ is 7·3. By choosing a heavier disk, say $I = 40{\cdot}2 \times 10^{-5}$, and a correspondingly thicker or shorter suspension so that S is also five times greater than before, the dynamic "sound-drift ratio" is improved five-fold. The absolute value of the dynamic sensitivity is unchanged, since $\frac{1}{R\omega}$ is the same as before.

From (1), (3), and (4) it is seen that for thin disks the dynamic sensitivity is independent of the disk radius, provided the disk period remains constant. The static sensitivity is proportional to the cube of the radius. The distinction is particularly important in high-frequency measurements, since the disk diameter must always be small in comparison with the sound wave-length.

On the other hand, it might be supposed that for low frequencies the static sensitivity can be greatly increased by choosing a as large as possible, subject only to $a<<\lambda$. Actually, however, two circumstances tend to offset (and sometimes more than offset) the advantage to be expected. Firstly, the time required for the static deflexion to settle down within a prescribed fraction of its final value. This time is proportional to $\frac{I}{R}$. Since I is proportional to a^4, and R is approximately proportional to a^3, the time required is proportional to a. Secondly, the sound-drift ratio may decrease quite rapidly as a increases. This would not be the case if the drift-torque were perfectly sustained, as in the sound-torque. Actually, the drift-torques observed in an enclosed box appear to be of two kinds:—

1. Slowly-fluctuating drifts, in effect containing alternating components of the order of 5 to 10 seconds per cycle. Such components are favoured, since their periods more nearly coincide with the free periods of the larger disks.

2. Short, sudden puffs of air, of the order of one second or less, which roughly may be regarded as torque impulses. The number of impulses received is proportional to the time required by the disk to settle down. And this time, as already pointed out, is approximately proportional to a.

Disturbance due to Double-frequency Amplitude.—Superposed on D_1, there is the amplitude D_2 of an oscillation with double the modulating frequency. For the particular disk described, $\frac{D_1}{D_2} = 66$. The effect of the 2ω term on the measurement of D_1 is seen to be rather small If the disk and suspension were altered as stated above, $\frac{D_1}{D_2}$ would be increased nearly fivefold, and the effect of D_2 rendered quite negligible.

Modulation of the Sound-wave. When the sound-source is electro-acoustic, it is only necessary to modulate the alternating current. Two methods have been used :—

(A) A resistance potentiometer to carry the sound-frequency current is wound on the periphery of a disk. A brush driven from a geared-down adjustable speed motor makes contact with the resistance units. The latter are so wound that the amplitude of the a.c. voltage tapped off by the brush varies in accordance with (1). The modulated voltage is impressed on an amplifier which feeds the sound-source.

(B) The sound-source is fed from two a.c. generators of equal amplitudes and nearly equal frequencies. The difference between the two frequencies is adjusted to equality with the natural frequency of the disk.

An error in the adjustment of ω will cause the observed D_1 to differ from its value in (3). It is easy to show that, for a given small percentage error in ω, the error in D_1 will be much less if ω is too low rather than too high.

Motional Resistance of Disk.—The value of R in (3) must be determined independently. The rate of decay of the free vibrations, $\epsilon^{-\frac{R}{2I}}$, is observed. This gives R, provided I is known. The latter can be computed from the mass and dimensions of the disk, $I = m\left(\frac{a^2}{4} + \frac{l^2}{12}\right)$. In the case of a small, fairly heavy disk (such as would normally be best fitted for the dynamic method) the moment of inertia which the air adds to the above value of I is quite negligible. But even in the case of a large light disk, the correct value of I is readily determined by observing the change in the free period caused by adding to the disk a known moment of inertia.

The above experimental determination of R is a simple matter. However, in selecting disk and suspension for any particular type of measurement, it is helpful to know R as a function of the disk dimensions, approximately at least. This function can be arrived at by regarding the disk as the limiting case of an ellipsoid. Suppose the ellipsoid $\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$ to rotate about the axis of X in an infinite viscous fluid. The motion is assumed to be so slow that the product of the velocities may be neglected. Then the couple

K, acting on the ellipsoid, is * :

$$K = \frac{32\mu\pi\omega(b^2+c^2)}{5(b^2B+c^2C)},$$

where

$$B = \int_0^\infty \frac{d\psi}{(b^2+\psi)P} \quad \text{and} \quad C = \int_0^\infty \frac{d\psi}{(c^2+\psi)P},$$

and

$$P = [(a^2+\psi)(b^2+\psi)(c^2+\psi)]^{\frac{1}{2}}.$$

For a thin circular disk we take $a=b$ and $c=0$. Evaluating the above integrals gives

$$K = \frac{64}{5}\mu a^2\omega \quad \text{and} \quad R = \frac{64}{5}\mu a^3.$$

The assumed smallness of ω is equivalent to the condition $\frac{\omega a^2\rho}{\mu} << 1$.

If the area of the disk-edge is not negligible, a first-order correction is obtained by regarding the surface of the edge as part of a sphere of radius a. The total resistance of a slowly-rotating sphere being $8\pi\mu a^3$, the resistance corresponding to the edge surface $(2\pi al)$ is $4\pi\mu a^2 l$. The following table gives a comparison of disk resistance computed from

$$R = \frac{64}{5}\mu a^3 + 4\pi\mu a^2 l$$

with those obtained from measurements on the rate of decay. The moments of inertia used in deducing the "observed" values of R were computed from the disk- and air-constants

$$I = m\left(\frac{a^2}{4}+\frac{l^2}{12}\right)+\frac{16}{45}\rho a^5$$

rather than directly measured.

a.	l.	R obs.	R calc.
0·15 cm.	0·026 cm.	$9{\cdot}64\times10^{-5}$	$9{\cdot}15\times10^{-6}$
0·254 ,,	0·11 ,,	$3{\cdot}55\times10^{-5}$	$3{\cdot}96\times10^{-5}$
0·316 ,,	0·052 ,,	$7{\cdot}96\times10^{-5}$	$8{\cdot}50\times10^{-5}$
0·476 ,,	0·03 ,,	$2{\cdot}62\times10^{-4}$	$2{\cdot}66\times10^{-4}$
0·479 ,,	0·0046 ,,	$2{\cdot}32\times10^{-4}$	$2{\cdot}57\times10^{-4}$
0·502 ,,	0·017 ,,	$2{\cdot}84\times10^{-4}$	$2{\cdot}96\times10^{-4}$

* D. Edwards, Quart. Journ. Pure and Appl. Math. xxvi. p. 70 (1893).

The added moment of inertia, $\frac{16}{45}\rho a^5$, is that for a disk rotating in an incompressible inviscid fluid *. Clearly, even for the slow vibrations of disks used in sound-measurements, both the resistance and moment of inertia due to the air are greater for the case of rotatory oscillations than the "steady rotation" values used above. A quantitative discussion of the air corrections for slow rotatory oscillations will be given elsewhere. For the purpose stated—to guide in selecting suitable disk-constants—the above expression for R is seen to be sufficiently accurate.

I am indebted to Mr. W. R. Goehner, of this laboratory, for his aid in conexion with the experimental part of this work.

Bell Telephone Laboratories, Inc., New York.
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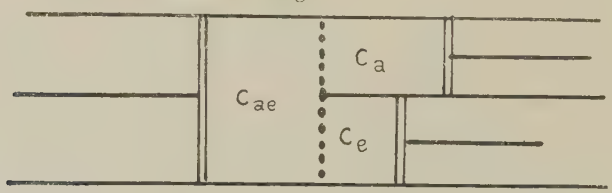
LXIII. *The Differential Equations of a Reacting Mixture.* *By* R. D. Kleeman, *B.A.*, *D.Sc.*†

WHEN a number of substances are mixed and they react chemically, the final state of equilibrium we would expect should be governed by a number of differential equations. These equations will be deduced in this paper.

Let us first consider a mixture consisting of M_a gram atoms of the substance a, and M_e gram atoms of the substance e, which combine to form various molecules. This mixture we will suppose is passed through an isothermal cycle by means of an apparatus shown diagrammatically in fig. 1. It consists of three adjacent chambers whose

Fig. 1.



* Lamb's 'Hydrodynamics,' 4th ed. p. 141.
† Communicated by the Author.

volumes may be varied by means of pistons—the chamber C is separated from the chamber C_{ae} by a membrane permeable to the molecules composed of the constituent a, and the chamber C_e is separated from the chamber C_{ae} by a membrane permeable to the molecules composed of the constituent e. The mixture is initially contained in the chamber C_{ae}. Now let us at constant temperature :—

(a) Transfer the mixture from the chamber C_{ae} into the chambers C_a and C_e, keeping the pressure p of the mixture and the pressures p_a and p_e of the substances a and e in the chambers C_a and C_e constant during the process. The external work done is equal to

$$M_a v_a p_a + M_e v_e p_e - vp,$$

where v denotes the initial volume of the mixture, and v_a and v_e the volumes of gram atoms of the substances a and e in the chambers C_a and C_e.

(b) Increase the volume of each of the chambers C_a and C_e by a small amount. The external work done is equal to

$$p_a M_a \cdot \partial v_a + p_e M_e \cdot \partial v_e.$$

(c) Return the substances to the chamber C_{ae} in the reverse way that they were separated, keeping the pressures in the chambers C_{ae}, C_a, and C_e constant during the process. This gives rise to the external work

$$-(M_a v_a p_a + M_e v_e p_e - vp) - \partial(M_a v_a p_a + M_e v_e p_e - vp).$$

(d) Compress the mixture until it has assumed its original volume. The external work done is

$$-p \cdot \partial v,$$

which completes the cycle.

On equating to zero the external work done, the equation

$$v\left(\frac{\partial p}{\partial v}\right)_{T, M_a, M_e} - M_a v_a \left(\frac{\partial p_a}{\partial v}\right)_{T, M_a, M_e} - M_e v_e \left(\frac{\partial p_e}{\partial v}\right)_{T, M_a\ M_e} = 0 \quad . \quad . \quad . \quad (1)$$

is obtained.

If the mixture contains the additional constituent c, the apparatus will involve an additional chamber separated from the chamber C_{ae} by a membrane permeable to the molecules composed of atoms c. The equation then contains the additional term

$$-M_c v_c \left(\frac{\partial p_c}{\partial v}\right)_{T, M_a, M_e, M_c},$$

and so on. It will also be recognized that similar equations may be obtained corresponding to each membrane being permeable to any given kind of molecule. These various equations evidently hold independently of the state of the mixture.

A set of equations similar to equation (1) may be obtained in each of which the mass of one of the constituents is the independent variable instead of the volume, by means of an isothermal cycle differing somewhat from the one just given. Thus let us:—

(*a*) Permit the transfer of a mass ∂M_a of the constituent a from the mixture into the chamber C_a, keeping the volume v of the mixture constant during the process. The external work done is

$$-p_a v_a \cdot \partial M_a.$$

(*b*) Transfer the mixture from the chamber C_{ae} into the chambers C_a and C_e, keeping the pressures in the chambers constant during the process. The external work done is

$$M_a v_a p_a + M_e v_e p_e - vp + \partial(M_a v_a p_a + M_e v_e p_e - vp).$$

(*c*) Change the volumes of the chambers C_a and C_e till the pressures of the substances they contain correspond to equilibrium with the mixture when it was completely contained in the chamber C_{ae}. The external work

$$-(M_a p_a \cdot \partial v_a + M_e p_e \cdot \partial v_e)$$

is obtained. The sign of this is negative because we are on the return path of the cycle.

(*d*) Return the substances in the chambers C_a and C_e to the chamber C_{ae}, keeping the pressures constant during the process. The external work done is

$$-(M_a v_a p_a + M_e v_e p_e - vp),$$

which completes the cycle. On equating the external work done to zero, we obtain *

$$\dot{v}\left(\frac{\partial p_e}{\partial M_a}\right)_{v,\,T,\,M_e} - M_a v_a \left(\frac{\partial p_a}{\partial M_a}\right)_{v,\,T,\,M_e} - M_e v_e \left(\frac{\partial p_e}{\partial M_a}\right)_{v,\,T,\,M_e} = 0. \quad \ldots \quad (2)$$

* It will be helpful if it is pointed out that we may first carry out the processes (*a*) and (*b*) of the cycle, then begin again with the mixture in the chamber C_{ae} and carry out the processes (*d*) and (*e*) in the reverse manner, beginning with (*d*) and equating the external work done in the two cases. Similar remarks apply to the previous cycle.

A similar equation holds referring to the constituent e, which may be obtained from equation (2) on substituting M_e for M_a. If the mixture contains the additional constituent c, equation (2) contains the additional term

$$-\left(\frac{\partial p_c}{\partial M_a}\right)_{v,\,T,\,M_e,\,M_c},$$

and an additional equation will hold in which the independent variable is M_c, and so on. These various equations apply to a mixture in any state.

One of the most important applications of the foregoing equations is in connexion with the equilibrium of a reacting gaseous mixture. Additional equations hold under these conditions. The pressure p of the mixture is given by

$$p = RT\Sigma C, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ΣC denotes the sum of the concentrations of the various molecules. Similarly, if p_1, p_2, ... denote the partial pressures of the various molecules which will be denoted by 1, 2, ..., and C_1, C_2, ... denote their concentrations, we have

$$\left.\begin{aligned} p_1 &= RT\,C_1, \\ p_2 &= RT\,C_2, \\ &\ldots \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The masses in gram atoms of the constituents a, e, ... are given by

$$\left.\begin{aligned} v\Sigma n_a C_a &= M_a, \\ v\Sigma n_e C_e &= M_e, \\ &\ldots \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C_a denotes the concentration in gram molecules of the molecules which contain n_a gram atoms a, C_e, the concentration of the molecules containing n_e gram atoms e etc. Lastly, we have the mass-action equation, which may be written in the generalized form

$$KC_1C_2 \ldots = C_4C_5 \ldots, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where K denotes the constant of mass action. The foregoing equations are the complete differential equations determining the equilibrium of a reacting gaseous mixture.

Let us apply them, for example, to a mixture reacting according to the equation

$$2ae \rightleftharpoons a_2 + e_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Equation (3) then gives

$$p = \mathrm{RT}(\mathrm{C}_{ae} + \mathrm{C}_{a_2} + \mathrm{C}_{e_2}), \quad . \quad . \quad . \quad . \quad (8)$$

where C_{ae}, C_{a_2}, and C_{e_2} denote the concentrations of the molecules ae, a_2, and e_2 respectively. Equations (4) and (5) give

$$\left.\begin{aligned} p_{ae} &= \mathrm{RT}\,\mathrm{C}_{ae}, \\ p_{a_2} &= \mathrm{RT}\,\mathrm{C}_{a_2}, \\ p_{e_2} &= \mathrm{RT}\,\mathrm{C}_{e_2}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\left.\begin{aligned} v(\mathrm{C}_{ae} + 2\mathrm{C}_{a_2}) &= \mathrm{M}_a, \\ v(\mathrm{C}_{ae} + 2\mathrm{C}_{e_2}) &= \mathrm{M}_e, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and equation (6)

$$\mathrm{K}\mathrm{C}_{ae}^2 = \mathrm{C}_{a_2}\mathrm{C}_{e_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Equation (1) may now be written

$$v\frac{\partial p}{\partial v} - \mathrm{M}_{a_2}v_{a_2}\frac{\partial p_{a_2}}{\partial v} - \mathrm{M}_{e_2}v_{e_2}\frac{\partial p_{e_2}}{\partial v} = 0, \quad . \quad . \quad (12)$$

where M_{a_2} and M_{e_2} denote the number of gram molecules of molecules a_2 and e_2, and v_{a_2} and v_{e_2} the volumes per gram molecule, respectively, into which the mixture can be separated. Since the molecules a_2 and e_2 do not dissociate when by themselves, we shall also have the gas equations

$$\left.\begin{aligned} v_{a_2}p_{a_2} &= \mathrm{RT}, \\ v_{e_2}p_{e_2} &= \mathrm{RT}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Now, from equations (8), (9), (10), (12), and (13) expressions can be obtained for the concentrations C_{ae}, C_{a2}, and C_{e_2} in terms of T, v, M_a, and M_e, and an arbitrary function of T, M_a, and M_e, where $2\mathrm{M}_{a_2} = \mathrm{M}_a$ and $2\mathrm{M}_{e_2} = \mathrm{M}_e$. If these are substituted in equation (11), it expresses the functional nature of K with respect to v.

It should be mentioned here that in a previous paper * the writer showed that K is in general a function of T, v, and the masses of the constituents instead of a function of T

* Phil. Mag. v. p. 263 (1928).

only, as has usually been accepted, but that in special cases, as we shall see presently, this may be the case. The equations obtained in this paper enable us to determine completely the functional nature of K *.

If equation (2) is applied to the reaction (7), it becomes

$$v\frac{\partial p}{\partial \mathrm{M}_{a_2}}-\mathrm{M}_{a_2}v_{a_2}\frac{\partial p_{a_2}}{\partial \mathrm{M}_{a_2}}-\mathrm{M}_{e_2}v_{e_2}\frac{\partial p_{e_2}}{\partial \mathrm{M}_{a_2}}=0. \quad . \quad (14)$$

Expressions for the molecular concentrations may now be obtained from equations (8), (9), (10), (13), and (14) in terms of T, v, M_a, and M_e, and an arbitrary function of T, v, and M_e, remembering that $2\mathrm{M}_{a_2}=\mathrm{M}_a$ and $2\mathrm{M}_{e_2}=\mathrm{M}_e$. If these expressions are substituted in equation (11), it expresses the functional nature of K with respect to M_a. Similarly, the functional nature of K with respect to M_e may be obtained.

Let us solve equations (13), (12), (11), (10), (9), and (8) for the special case corresponding to $\mathrm{M}_a=\mathrm{M}_e$, or $\mathrm{M}_{a_2}=\mathrm{M}_{e_2}$, in which also $p_{a_2}=p_{e_2}$ and $\mathrm{C}_{a_2}=\mathrm{C}_{e_2}$. Equation (8) may then be written $p=\mathrm{RT}\,\mathrm{M}_a/v$ by means of equations (10). From this equation and equations (13), (12), and (9) we then have

$$\frac{1}{v}+\frac{1}{\mathrm{C}_{a_2}}\frac{\partial \mathrm{C}_{a_2}}{\partial v}=0.$$

The solution of this equation is

$$\mathrm{C}_{a_2}=\frac{\phi(\mathrm{T},\ \mathrm{M}_a,\ \mathrm{M}_e)}{v}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where ϕ is an arbitrary function of T, M_a, and M_e. From this equation and equations (11) and (10) we then have

$$\mathrm{K}=\frac{\phi^2}{(\mathrm{M}_a-2\phi)^2}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Thus in this particular case K is not a function of v, which agrees with the experiments that have been carried out on the dissociation of hydriodic acid. The case corresponding to M_a not being equal to M_e is more complicated.

* Provided the perfect gas equation has the form $pv=\mathrm{MRT}$. Thermodynamics has something to state in this connexion, which will be pointed out in a subsequent paper. It need not concern us for the present.

From equations (8) and (10) we have

$$p = \mathrm{RT}\frac{(\mathrm{M}_a+\mathrm{M}_e)}{2v}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\mathrm{C}_{a_2}-\mathrm{C}_{e_2}=\frac{\mathrm{M}_a-\mathrm{M}_e}{2v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

By means of equations (17), (13), and (9) we may write equation (12)

$$\frac{\mathrm{M}_a+\mathrm{M}_e}{2v}+\frac{\mathrm{M}_{a_2}}{\mathrm{C}_{a_2}}\frac{\partial \mathrm{C}_{a_2}}{\partial v}+\frac{\mathrm{M}_{e_2}}{\mathrm{C}_{e_2}}\frac{\partial \mathrm{C}_{e_2}}{\partial v}=0. \quad . \quad . \quad (19)$$

Let us write $\mathrm{C}_{a_2}=y/v$ and $\mathrm{C}_{e_2}=z/v$ in this equation and equation (18), and they become

$$2(y+z) = \mathrm{M}_a-\mathrm{M}_e, \quad . \quad . \quad . \quad . \quad (20)$$

$$\frac{\mathrm{M}_{a_2}}{y}\frac{\partial y}{\partial v}+\frac{\mathrm{M}_{e_2}}{z}\frac{\partial z}{\partial v}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

It is evident from these equations that y and z are functions of T, M_a, and M_e only. It can now easily be shown that

$$\mathrm{K}(\mathrm{M}_a-2y)^2 = yz, \quad , \quad . \quad . \quad . \quad . \quad , \quad (22)$$

and thus K is not a function of v. This agrees with the experiments on the equilibrium of reacting mixtures of H_2 and I_2 in various proportions.

Let us next consider a gaseous reaction proceeding according to the equation

$$ae \rightleftharpoons a+e. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

According to equations (3), (4), (5), and (6) we then have

$$p = \mathrm{RT}(\mathrm{C}_{ae}+\mathrm{C}_a+\mathrm{C}_e), \quad . \quad . \quad . \quad (24)$$

$$\left.\begin{aligned} p_{ae} &= \mathrm{RT}\,\mathrm{C}_{ae},\\ p_a &= \mathrm{RT}\,\mathrm{C}_a,\\ p_e &= \mathrm{RT}\,\mathrm{C}_e, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$\left.\begin{aligned} v(\mathrm{C}_{ae}+\mathrm{C}_a) &= \mathrm{M}_a,\\ v(\mathrm{C}_{ae}+\mathrm{C}_e) &= \mathrm{M}_e, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\mathrm{K}\mathrm{C}_{ae} = \mathrm{C}_a\mathrm{C}_e. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Since the molecules a and e when by themselves do not dissociate, we also have the gas equations

$$\left.\begin{aligned} v_a p_a &= \mathrm{RT}, \\ v_e p_e &= \mathrm{RT}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Let us consider the special case corresponding to $\mathrm{M}_e = \mathrm{M}_a$, in which case also $p_a = p_e$ and $\mathrm{C}_a = \mathrm{C}_e$. Equation (24) may then be written

$$p = \mathrm{RT}\left(\frac{\mathrm{M}_a}{v} + \mathrm{C}_a\right).$$

From this equation and equations (1), (28), and (25) it can then be deduced that

$$-\frac{\mathrm{RT\,M}_a}{v} + \mathrm{RT}\,v\frac{\partial \mathrm{C}_a}{\partial v} - \frac{2\mathrm{RT\,M}_a}{\mathrm{C}_a}\frac{\partial \mathrm{C}_a}{\partial v} = 0,$$

or

$$\frac{\partial \mathrm{C}_a}{\partial v} = \frac{\mathrm{M}_a}{v}\left(\frac{\mathrm{C}_a}{\mathrm{C}_a v - 2\mathrm{M}_a}\right). \quad . \quad . \quad . \quad . \quad (29)$$

Instead of solving this equation we may proceed in a somewhat different way, which is shorter. Let us write equation (27) in the form

$$\mathrm{K}\left(\frac{\mathrm{M}_a}{v} - \mathrm{C}_a\right) = \mathrm{C}_a{}^2 \quad . \quad . \quad . \quad . \quad . \quad (30)$$

by means of equation (26), and differentiate it with respect to v, supposing K not a function of v, which gives

$$-\mathrm{K}\left(\frac{\mathrm{M}_a}{v^2} + \frac{\partial \mathrm{C}_a}{\partial v}\right) = 2\mathrm{C}_a\frac{\partial \mathrm{C}_a}{\partial v}.$$

On eliminating $\dfrac{\partial \mathrm{C}_a}{\partial v}$ and K from this equation by means of equations (29) and (30) the equation identically vanishes. Thus the supposition made is true, or K is not a function of v. This is borne out by experiments on the dissociation of nitrogen tetroxide ($\mathrm{N_2O_4}$).

Further cases may be found for which K is not a function of v. Let us consider a reaction proceeding according to the equation

$$2ae_2 \rightleftarrows 2ae + e_2. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

The equations corresponding to equations (3) and (4) are

$$p = \mathrm{RT}(\mathrm{C}_{ae_2} + \mathrm{C}_{ae} + \mathrm{C}_{e_2}), \quad . \quad . \quad . \quad (32)$$

$$\left.\begin{aligned} p_{ae_2} &= \mathrm{RT}\,\mathrm{C}_{ae_2}, \\ p_{ae} &= \mathrm{RT}\,\mathrm{C}_{ae}, \\ p_{e_2} &= \mathrm{RT}\,\mathrm{C}_{e_2}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

and the equations corresponding to equations (5), (6), and (1) are

$$\left.\begin{aligned} \mathrm{C}_{ae_2} + \mathrm{C}_{ae} &= \mathrm{M}_a/v, \\ 2\mathrm{C}_{ae_2} + \mathrm{C}_{ae} + 2\mathrm{C}_{e_2} &= \mathrm{M}_e/v, \end{aligned}\right\} \quad . \quad . \quad . \quad (34)$$

$$\mathrm{K}\mathrm{C}_{ae_2}^2 = \mathrm{C}_{ae}^2\mathrm{C}_{e_2}, \quad . \quad . \quad . \quad . \quad . \quad (35)$$

$$v\frac{\partial p}{\partial v} - \mathrm{M}_{ae}v_{ae}\frac{\partial p_a}{\partial v} - \mathrm{M}_{e_2}v_{e_2}\frac{\partial p_{e_2}}{\partial v} = 0. \quad . \quad . \quad (36)$$

Since the molecules *ae* and e_2 are supposed to remain unchanged when by themselves, we also have

$$\left.\begin{aligned} p_{ae}v_{ae} &= \mathrm{RT}, \\ p_{e_2}v_{e_2} &= \mathrm{RT}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Let us consider the special case corresponding to $2\mathrm{M}_a = \mathrm{M}_e$. From equations (34) we then have

$$\mathrm{C}_{ae} = 2\mathrm{C}_{e_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

and from this equation and equations (34), (32), (33), and (35) we have

$$p = \mathrm{RT}\left(\frac{\mathrm{M}_e}{2v} + \mathrm{C}_{e_2}\right), \quad . \quad . \quad . \quad . \quad (39)$$

$$\left.\begin{aligned} p_{ae} &= \mathrm{RT}\,2\mathrm{C}_{e_2}, \\ p_{e_2} &= \mathrm{RT}\,\mathrm{C}_{e_2}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

$$\mathrm{K}\mathrm{C}_{ae_2}^2 = 4\mathrm{C}_{e_2}^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

taking into account that

$$\left.\begin{aligned} \mathrm{M}_{ae} = \mathrm{M}_a &= \mathrm{M}_e/2, \\ 2\mathrm{M}_{e_2} + \mathrm{M}_{ae} &= \mathrm{M}_e. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (42)$$

Equation (36) may now be written

$$RT\left\{-\frac{M_e}{2v}+v\frac{\partial C_{e_2}}{\partial v}\right\}-\frac{3}{4}\frac{RT\,M_e}{C_{e_2}}\frac{\partial C_{e_2}}{\partial v}=0,$$

or

$$\frac{\partial C_{e_2}}{\partial v}=\frac{M_e}{v}\frac{2C_{e_2}}{4C_{e_2}v-3M_e}, \quad . \quad . \quad . \quad . \quad (43)$$

by means of equations (39), (40), (41), and (42).

From equations (34), (38), and (42) we have

$$C_{ae_2}=\frac{M_e}{2v}-2C_{e_2}. \quad . \quad . \quad . \quad . \quad . \quad (44)$$

On differentiating equation (41) with respect to v, supposing K *not* a function of v, it may be written

$$-2KC_{ae_2}\left\{\frac{M_e}{2v^2}+\frac{2\partial C_{e_2}}{\partial v}\right\}=12C_{e_2}^2\frac{\partial C_{e_2}}{\partial v}$$

by means of equation (44). It reduces to

$$\frac{-KC_{ae_2}M_e}{v^2}\left\{\frac{12Cv_e-3M_e}{4C_{e_2}v-3M_e}\right\}=\frac{24M_e}{v}\frac{C_{e_2}}{4C_{e_2}v-3M_e}$$

by means of equation (43). Eliminating C_{e_2} by means of equation (41), and then C_{ae_2} by means of equation (44), the equation reduces to zero.

Hence the supposition made is true, or K is not a function of v. This result will apply to the well-known reactions

$$2CO_2 \rightleftharpoons 2CO+O_2, \quad . \quad . \quad . \quad . \quad (45)$$

$$2NO_2 \rightleftharpoons 2NO+O_2. \quad . \quad . \quad . \quad . \quad (46)$$

The various results obtained fall into line with the general result obtained in a previous paper, that the constant of mass action is in general a function of T, v, and the masses of the constituents, but that in special cases it may be a function of the temperature only. It is also evident that the functional nature of the constant of mass action is in all cases determined by equations of the type given. The subject admits of considerable further development, which will be carried out in subsequent papers.

LXIV. *On Approximate Theories of Diffusion Phenomena.* *By* S. Chapman, *M.A., D.Sc., F.R.S.**

1. THE object of this note is to draw attention to the erroneous character of an argument often used in approximate theories of diffusion phenomena. It is the basis of Meyer's theory of diffusion [1], which is now about fifty years old, and is generally reproduced, with modifications not affecting the error here described, in modern text-books on the kinetic theory of gases. The argument has recently been used in an attempt to explain the Soret phenomenon in liquids [2].

2. In some cases it leads to results which are qualitatively correct in certain respects, but other no less valid applications of it can be found in which it predicts phenomena that either do not occur (§ 7), or are inconsistent with the initial hypotheses (§ 8), or which, though of an observed kind, are deduced with the wrong sign (§ 9). It is therefore unsafe to use it in searching for new phenomena, and scarcely satisfactory to make it the basis of a theory, even in cases where it gives approximately correct results—better no simple theory than one based on unsafe or erroneous arguments.

3. Diffusion phenomena can be most simply considered with reference either to steady diffusive flow, in which all the properties of the system at every point remain constant: or to the maintenance of a steady state in which no diffusion occurs because two separate causes each tending to produce it are balanced against one another. An instance of the latter is the equilibrium of a mixed fluid subject to gravity; the heavier component is in excess in the lower strata, but its preponderance is limited by the tendency of diffusion towards a uniform mixture. Likewise, if there is a gradient of temperature along a tube containing a mixed gas, one set of molecules (usually the lighter) will diffuse towards the hotter regions, until a steady state is attained in which there is a gradient of concentration sufficient to neutralize further thermal diffusion [3]. A similar process occurs in mixed liquids, and is known as the Soret effect.

4. The argument will first be considered in relation to steady states of the second kind. Let there be two sorts of

* Communicated by the Author.

molecules (1, 2), of masses m_1, m_2, numbers per unit volume n_1, n_2, mean speeds C_1, C_2. We write

$$n=n_1+n_2, \quad c_1=n_1/n, \quad c_2=n_2/n, \quad . \quad . \quad . \quad (1)$$

so that

$$c_1+c_2=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Pressure and absolute temperature will be denoted by p and T; then

$$m^1C_1^2=m_2C_2^2=a\mathrm{T}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a is a universal constant.

5. Suppose there is a temperature gradient along the direction of z, the pressure being uniform. The argument states that the number of molecules (1) which cross any plane of constant z, per unit area per unit time, in the positive direction, is $k(n_1C_1)_{z-\lambda_1}$, where k is a numerical constant, while the suffix implies that the value of n_1C_1 is that at the plane $z-\lambda_1$, at a distance λ_1 on the negative side of the plane z; λ_1 is a multiple of the mean free path of the molecules (1), by a factor which, like k, is independent of the nature of the gas and of the variables of state. Similarly, the rate of flow in the opposite direction is $k(n_1C_1)_{z+\lambda_1}$. The gas being in a steady state of equilibrium, there being no resultant diffusion, these two quantities must be equal, and therefore n_1C_1 is independent of z. Hence, by (3), $n_1\mathrm{T}^{\frac{1}{2}}$ is constant along the tube [2].

This simple and general argument applies to either a liquid or a gas, and to each kind of molecule in a mixture. Hence it indicates that for the molecules (2) likewise, $n_2\mathrm{T}^{\frac{1}{2}}$ is constant. Consequently $n_1\mathrm{T}^{\frac{1}{2}} : n_2\mathrm{T}^{\frac{1}{2}}$ or $n_1 : n_2$ is independent of z, so that there can be no gradient of concentration. This is contrary to the facts.

6. The argument must therefore be wrong in regard to one or both of the constituents; the experiments of C. C. Tanner [4] on the Soret effect have shown [2] that in the case of an aqueous solution of KCl (taken as substance 1) $n_1\mathrm{T}^{\frac{1}{2}}$ is nearly constant over the temperature range of the observations; but the existence of a concentration gradient shows that $n_2\mathrm{T}^{\frac{1}{2}}$ cannot also be constant. The agreement in the case of KCl can only be regarded as accidental, and indeed other substances fail to show it.

Since this method of attempting to explain the Soret effect is unsound as well as unsuccessful, it is to no purpose to attribute the failure of constancy of $n_1\mathrm{T}^{\frac{1}{2}}$ in other cases

to ionization; particularly since in gases a concentration gradient is set up by temperature differences in cases where there is certainly no appreciable ionization (*cf.* the experiments of T. L. Ibbs [5] on thermal diffusion in mixtures of argon and helium, and other gases).

7. The argument of § 5 is equally applicable to a *simple* gas at rest, in which a temperature gradient is maintained. The result is the same, that $n\mathrm{T}^{\frac{1}{2}}$ is constant, whereas in fact, since the pressure is uniform, $n\mathrm{T}$ is constant, *i. e.* $n\mathrm{T}^{\frac{1}{2}} \propto \mathrm{T}^{-\frac{1}{2}}$.

8. Analogous discrepancies with fact occur when the argument is used in relation to states of steady diffusion. The ordinary case (I.) is that in which p and T are uniform, while c_1, c_2 vary. Other important cases are those in which c_1 and c_2 are uniform, while (II.) T varies and p is uniform or (III.) p varies and T is uniform; case II. is that of thermal diffusion, case III. that of pressure diffusion.

In all three cases we will suppose that there is no resultant flow of molecules across any stationary plane. Let ν_1, ν_1' be the numbers of molecules (1) flowing per unit area per unit time across such a plane, in the positive and negative directions respectively; and let ν_2, ν_2' have similar significance for the molecules (2). Then the stated condition implies

$$\nu_1+\nu_2=\nu_1'+\nu_2' \quad \text{or} \quad \nu_1-\nu_1'=-(\nu_2-\nu_2'); \quad . \quad (4)$$

i. e., the net rates of flow for the two kinds are equal and opposite. The velocity of diffusion, w_{12}, and the coefficient of diffusion D_{12}, are defined by

$$nw_{12}=\nu_1-\nu_1'=-n\mathrm{D}_{12}\frac{dc_1}{dz}, \quad nw_{12}=-(\nu_2-\nu_2') = -n\mathrm{D}_{12}\frac{dc_2}{dz}, \quad . \quad . \quad . \quad (5)$$

which are consistent since, by (2),

$$\frac{dc_1}{dz}=-\frac{dc_2}{dz}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It may be noted that, if the molecular masses are unequal, there is a resultant flow of *mass* across the plane z. This is given by

$$m_1(\nu_1-\nu_1')+m_2(\nu_2-\nu_2')=(m_1-m_2)(\nu_1-\nu_1'),$$

by (4).

The "mean mass-velocity" w is defined by

$$w=(m_1-m_2)(\nu_1-\nu_1')/n. \quad . \quad . \quad . \quad . \quad (7)$$

9. In Meyer's theory of diffusion due to a concentration gradient (case I.) it is assumed in effect that for each constituent the molecular velocities are distributed about this mean velocity w approximately in the Maxwellian manner; this is true, but the small deviation, which is neglected, is the essence of the phenomenon, and vital to any satisfactory theory of it. Further, Meyer assumed that the rate of flow of molecules (1) across a plane moving with the velocity w was

$$k(n_1C_1)_{z-\lambda_1} - k(n_1C_1)_{z+\lambda_1}, \quad \text{or} \quad -2k\lambda_1 \frac{d(n_1C_1)}{dz} \quad . \quad (8)$$

much as in § 5. To get $\nu_1 - \nu_1'$, the rate of net flow of molecules (1) across a stationary plane, we must add $n_1 w$, so that

$$\nu_1 - \nu_1' = n_1 w - 2k\lambda_1 C_1 \frac{dn_1}{dz}, \quad . \quad . \quad . \quad . \quad (9)$$

since T and therefore C_1, C_2 (*cf.* 3) are constant in case I. Likewise

$$\nu_2 - \nu_2' = n_2 w - 2k\lambda_2 C_2 \frac{dn_2}{dz} = n_2 w + 2k\lambda_2 C_2 \frac{dn_1}{dz} \quad . \quad (10)$$

if, as in a perfect gas at uniform pressure, $n_1 + n_2$ is constant.

The usual procedure is to eliminate w from (9), (10) by means of (4). This gives

$$\nu_1 - \nu_1' = -(\nu_2 - \nu_2') = -(2k/n)(n_2\lambda_1 C_1 + n_1\lambda_2 C_2)\frac{dn_1}{dz}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or, comparing with (5), and remembering that n is constant, so that $n dc_1/dz = dn_1/dz$,

$$D_{12} = (2k/n)(n_2\lambda_1 c_1 + n_1\lambda_2 C_2). \quad . \quad . \quad . \quad (12)$$

Different authors have given different estimates of the constant k and of the appropriate mean free paths λ_1, λ_2, in some cases taking into account the persistence of velocities after collision [6]; this step undoubtedly produces a better value of D_{12}, but it should be noted that the formula (12) is deduced from a set of equations that are inconsistent with one another, so that however refined the methods of calculation of λ_1 and λ_2 may be, the result must be unsatisfactory. The inconsistency appears on deducing w from (4), (9), (10), giving

$$w = \frac{2k}{n_1 - n_2}(\lambda_1 C_1 - \lambda_2 C_2)\frac{dn_1}{dz}, \quad . \quad . \quad . \quad (13)$$

which is incompatible with (7). The disagreement is

particularly obvious when $m_1=m_2$, for then $w=0$ (*cf.* 7), and $C_1=C_2$ (*cf.* 3) ; (9) and (10) are compatible with (4) only if $\lambda_1=\lambda_2$, which is untrue, on any reasonable definitions of the λ's, if the molecular diameters are unequal.

Gross[7] criticized Meyer's deduction of (12) on different grounds, and proposed the alternative formula $D_{12}=k(\lambda_1C_1+\lambda_2C_2)$, but without any proper justification ; this formula, like (12), is known to be incorrect.

10. Similar contradictions with the initial hypotheses, and with fact, arise when the same method of argument is applied, as one is tempted to do, to explain the steady diffusive flow in cases II. and III. (§ 8), which can be treated together. In (8) C_1 is no longer independent of z ; writing $n_1=c_1n$, where c_1 but not n is independent of z, we get, analogous to (9), (10),

$$\nu_1-\nu_1'=n_1w-2k\lambda_1C_1\frac{dnC_1}{dz}, \quad . \quad . \quad . \quad . \quad (14)$$

$$\nu_2-\nu_2'=n_2w-2k\lambda_2C_2\frac{dnC_2}{dz}. \quad . \quad . \quad . \quad . \quad (15)$$

In a perfect gas $n\propto p\mathrm{T}$, so that, also using (3), we have

$$\nu_1-\nu_1'=n_1w-k'(\lambda_1c_1/m_1^{\frac{1}{2}})\frac{d(p\mathrm{T}^{-\frac{1}{2}})}{dz}, \quad . \quad . \quad (16)$$

$$\nu_2-\nu_2'=n_2w-k'(\lambda_2c_2/m_2^{\frac{1}{2}})\frac{d(p\mathrm{T}^{-\frac{1}{2}})}{dz}, \quad . \quad . \quad (17)$$

where k' is another numerical constant independent of the nature and state of the constituents. Case II. corresponds to p constant, T variable, and *vice versâ* for case III.

As in § 9, (16) and (17) are incompatible with (4) and (7). Their erroneous character is specially obvious when $m_1=m_2$, with its corollary $w=0$; for then $\nu_1-\nu_1'$, $\nu_2-\nu_2'$ are both of the same sign, and proportional to λ_1c_2 and λ_2c_2 respectively, so that for both reasons they cannot satisfy (4). As applied to case II. they imply that both sets of molecules should diffuse in the same direction ; either (16) or (17) must be wrong in sign, and therefore in error by more than its whole amount. As regards case III., it is known that when $m_1=m_2$, $\nu_1-\nu_1'$ and $\nu_2-\nu_2'$ vanish; this again is not in accordance with (16) and (17). Hence this method of argument cannot be applied to explain either thermal diffusion or the simpler process of diffusion due to a pressure gradient.

11. The correct theory of these various diffusion phenomena depends on the determination of the velocity distribution function, which in non-uniform states deviates slightly from the Maxwellian form. In case II., for example, the function, for the velocity u_1, v_1, w_1, of a typical molecule (1), relative to the mean numerical velocity of all the molecules (without regard to mass) at any point, is easily shown to be

$$f_1\left\{1+\left(u_1\frac{\partial \mathrm{T}}{\partial x}+v_1\frac{\partial \mathrm{T}}{\partial y}+w_1\frac{\partial \mathrm{T}}{\partial z}\right)\phi_1(u_1^2+v_1^2+w_1^2)\right\} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

to a first approximation, where f_1 is the Maxwellian function for the constituent (1), while ϕ_1 is a function depending on the nature and proportions of the two gases; (18) reduces to f_1 when T is uniform. The velocity of diffusion in the z direction is the mean value of w_1, *i.e.*,

$$w_{12}=\frac{d\mathrm{T}}{dz}\int\int\int w_1^2 J_1\phi_1\, du_1\, dv_1\, dw_1\,; \quad . \quad . \quad (19)$$

there is a similar expression for the mean value of w_2, which must equal $-w_{12}$. This is one of the conditions which ϕ_1 and ϕ_2 have to satisfy. These considerations establish the expectation that a thermal gradient in an otherwise uniform gas will set up a diffusive flow, though the actual determination of ϕ_1, ϕ_2 and w_{12} is a very difficult matter. In spite of many attempts I have failed to find any simple arguments on which to base an easy approximate theory of thermal diffusion.

12. In conclusion, it may be noted that steady diffusive flow in a cylindrical tube requires that w_{12} shall be constant along the tube. In cases I., II., III. respectively this implies the constancy of

$$\mathrm{D}_{12}\frac{dc_1}{dz},\quad \mathrm{D}_\mathrm{T}\frac{d\mathrm{T}}{dz},\quad \mathrm{D}_p\frac{dp}{dz},$$

where D_T, D_p are the coefficients of thermal diffusion and pressure diffusion. In general, in the given circumstances, the coefficients will vary along the tube in a definite manner, D_{12} depending on c_1 and c_2, D_T on T, and D_p on p. Hence the gradients of c_1, p, and T cannot be arbitrary. In case I. the concentration gradient will vary along the tube so as to render $\mathrm{D}_{12}\,dc_1/dz$ constant; cases II. and III. are possible

only if p and T are imposed so as to satisfy the condition of continuity—otherwise this condition will be secured, in a state of steady flow, by an accompanying variation of c_1 and c_2 along the tube.

References.

(1) Meyer's 'Kinetic Theory of Gases' (English translation), p. 255.
(2) Trans. Faraday Soc. xxiii. p. 314 (1927).
(3) D. Enskog, *Phys. Zeit.* xii. p. 538 (1911); *Ann. d. Phys.* xxxviii. p. 742 (1912); Dissertation, Uppsala, 1917; *Arkiv f. Nat. Astro. o. Fysik*, xvi. (1921). S. Chapman, Proc. Roy. Soc. A, xciii. p. 1 (1916); Phil. Trans. A, ccxvii. p. 157 (1917). S. Chapman and F. W. Dootson, Phil. Mag. xxxiii. p. 268 (1917).
(4) C. C. Tanner, Trans. Faraday Soc. xxiii. p. 91 (1927).
(5) T. L. Ibbs, Proc. Roy. Soc. xcix. p. 385 (1921); *ib.* cvii. p. 470 (1925); Proc. Phys. Soc. xxxix. p. 227 (1927). *Cf.* also Elliott and Masson, Proc. Roy. Soc. A. cviii. p. 378 (1925).
(6) J. P. Kuenen, *Comm. Phys. Lab. Leiden*, Jan. 1913, Suppls. 28 & 38. Also J. H. Jeans, 'Dynamical Theory of Gases,' ch. xiii.
(7) Gross, *Annalen der Physik*, xl. p. 424 (1890).

LXV. *A Note on the Problem of the "Mass" of a Moving Electron.* *By* T. J. I'A. Bromwich *.

* Communicated by the Author.

AS far as I am aware, the only *direct* evidence of the Lorentz formula for the "*mass*" of an electron (moving with velocity v), namely

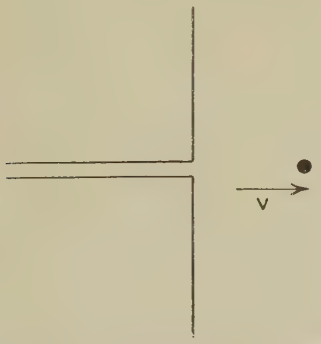
$$m = m_0/\sqrt{(1-\beta^2)} \quad \text{if } \beta = v/c,$$

where c is the velocity of radiation, is derived from Bucherer's experiments (and similar experiments conducted later). The mathematical treatment of Lorentz consists in replacing the *moving* particle by a *fixed* particle; this led Lorentz to the familiar Larmor-Lorentz transformation, afterwards used by Einstein as the basis of his theory of Relativity.

Now, in the actual experiment the particles of radium pass through a narrow slit between the two faces of a condenser. We can make the problem a little more manageable by treating the condenser as composed of two large conducting blocks with plane faces, at different potentials—as in fig. 1.

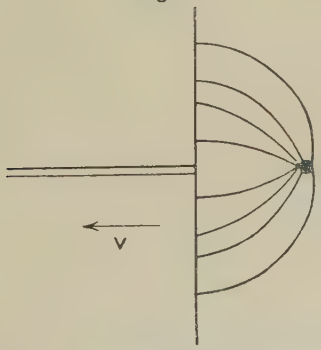
If we apply the Lorentz transformation to this diagram (ignoring the slit), we obtain a similar figure (fig. 2) in which the condenser moves and the particle is at rest.

Fig. 1.



Here the lines of force (although complicated in actual fact) cannot differ very greatly from those in the corresponding *electrostatic* problem. On account of the potential difference of

Fig. 2.



the two plates of the condenser, it is evident that the lines *cannot* be symmetrical about the horizontal plane (although the principal deviation from symmetry is due to the fact that the condenser is on the *left* of the particle).

Now, Lorentz assumes that the particle is so far from the condenser that all deviations from symmetry can be ignored : otherwise the formulæ become hopelessly complicated.

It would therefore seem that the Lorentz formula for m/m_0 can be applied safely only when the distance of the electron from the condenser is large compared with the radius of the electron. A consideration of the approximate dimensions shows that the deviations in Bucherer's experiments can be

calculated by Lorentz's method with sufficient accuracy: but that does not justify the argument that β can never be equal to 1.

In the case $v=c$ ($\beta=1$), two simple problems can be worked out by Heaviside's methods; these seem sufficiently near to the experimental results to be worth noticing here.

First suppose that $v=c$ ($\beta=1$) and that the particle is moving parallel to a conducting plate at zero potential—this corresponds to the assumption that the electron is between the two plates, while the upper plate is far enough away to be ignored.

The problem is then the same as the electrostatic problem of a circular cylinder above a plane at zero potential; thus the lines of electric force are arcs of coaxial circles, and these are cut orthogonally by the lines of magnetic force.

Secondly, suppose that the particle is moving with speed $v=c$ *at right angles* to a plane at zero potential. This corresponds to the assumption that the whole condenser can be replaced by one plane; this problem (for a point-charge) is actually worked out in vol. i. of Heaviside's 'Electromagnetic Theory' (p. 62). It is then easy to verify that all the conditions of the problem are satisfied by assuming the lines of force to be circular—with a centre at the point representing the slit in the condenser.

The transverse electric force is found to be equal to *

$$Q/(ar\sin\theta),$$

using spherical polar coordinates (so that $r=0$ gives the slit and $\theta=\pi/2$ gives the plane conductor). The resultant force on the electron is equal to

$$Q^2/avt$$

(where t is the time since the centre of the electron left the slit).

Also the energy is equal to †

$$\frac{Q^2}{a}\left\{\log\left(\frac{vt}{a}\right)+1\right\}.$$

[Since the above note was written out for the press, news of the death of H. A. Lorentz has reached me; I had hoped to submit these ideas for his comments, but it is now too late to do more than record a personal feeling of regret.—T. J. I'a. B.]

13th Feb., 1928.

* A slight modification is necessary at points *inside* the electron.

† It may be worth while to note that (under ordinary experimental conditions) the value of the bracket varies between 1 and 30, roughly.

LXVI. *The Relativistic Rule for Equipartition of Energy.* (Further note.) *By* F. F. P. Bisacre, *M.A.*, *O.B.E.**

IN my previous note on this subject, I concluded that

$$\bar{\epsilon} \rightarrow \tfrac{2}{3}\,\mathrm{RT} \quad \text{as} \quad \mathrm{T} \rightarrow \infty,$$

or

$$\bar{\epsilon} \rightarrow \mathrm{RT} \quad \text{as} \quad \mathrm{T} \rightarrow \infty,$$

depending on whether we take $\tau\beta^4$ or $\tau\beta^5$ as the volume of the cell of "equal *a priori* probability" †.

The problem can be presented in a way that seems to point decisively to the latter hypothesis as the correct one.

Boltzmann's probability-theory proceeds on the assumption that, if we use Hamiltonian coordinates and measure the element of volume in the generalized (p, q) diagram by

$$d\mathrm{V} = dq_1\, dq_2\, dq_3\, dp_1\, dp_2\, dp_3,$$

the distribution of representative points in the (p, q) diagram, over equal elements, can be determined by Boltzmann's lottery. The (p, q) diagram and not the $(\dot{q}, q)$ diagram must, in general, be used in order that the results shall be independent of the particular system of coordinates used.

If, for instance, we can define the state of the particle by the coordinates $q_1, q_2, q_3, \alpha_1, \alpha_2, \alpha_3$, and $q_1', q_2', q_3', \alpha_1', \alpha_2', \alpha_3'$, as alternative coordinate systems at rest with respect to each other, then the element of volume $dq_1 \ldots d\alpha_3$ is equal to the element $dq_1' \ldots d\alpha_3'$ if the Jacobian

$$\frac{\mathrm{D}(q_1, q_2, q_3, \alpha_1, \alpha_2, \alpha_3)}{\mathrm{D}(q_1', q_2', q_3', \alpha_1', \alpha_2', \alpha_3')} = 1.$$

This Jacobian is unity if $\alpha_1, \alpha_2, \alpha_3$ are defined by the equations

$$\alpha_1 = \frac{\partial \mathrm{T}}{\partial \dot{q}_1}, \quad \ldots\ldots, \quad \alpha_3 = \frac{\partial \mathrm{T}}{\partial \dot{q}_3},$$

where T is a function of $q_1, q_2, q_3, \dot{q}_1, \dot{q}_2, \dot{q}_3$, which is an invariant quantity of the alternative coordinate systems ‡.

Such a function exists in particle dynamics of the special theory of relativity; for, if we identify the α's with the *momenta*, p_1, p_2, p_3, the equations

$$p_1 = \frac{\partial \mathrm{T}}{\partial \dot{q}_1}, \quad \ldots\ldots, \quad p_3 = \frac{\partial \mathrm{T}}{\partial \dot{q}_3}$$

* Communicated by the Author.

† $\beta = (1 - v^2/c^2)^{-\frac{1}{2}}$.

‡ For details of the proof, see Lorentz, 'Lectures on Theoretical Physics,' vol. ii. p. 150. (Macmillan, 1927.)

hold good where

$$T = m_0 c^2 \left\{ 1 - \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}} \right\},$$

which is obviously invariant, as it depends only on the velocity, v, and constants. It is not the kinetic energy, however.

The conclusion of all this is that the calculation should be based, fundamentally, on a momentum diagram * (where all the coordinates can and do go to infinity). If we use a velocity diagram, we must apply a correcting factor to the element of volume of this diagram.

If the momentum coordinates are p_1, p_2, p_3, and the velocity coordinates $\dot{q}_1$, $\dot{q}_2$, $\dot{q}_3$, we have

$$dp_1\, dp_2\, dp_3 = \frac{D(p_1, p_2, p_3)}{D(\dot{q}_1, \dot{q}_2, \dot{q}_3)}\, d\dot{q}_1\, d\dot{q}_2\, d\dot{q}_3.$$

The correcting factor is therefore

$$\frac{D(p_1, p_2, p_3)}{D(\dot{q}_1, \dot{q}_2, \dot{q}_3)},$$

where

$$p_1 = m_0 \dot{q}_1 \left\{ 1 - \frac{v^2}{c^2} \right\}^{-\frac{1}{2}} = m_0 \beta \dot{q}_1,$$

$$p_2 = m_0 \beta \dot{q}_2,$$

$$p_3 = m_0 \beta \dot{q}_3,$$

and it turns out that the value of this Jacobian is $m_0^3 \beta^5$;

$$\text{i. e.,} \qquad dp_1\, dp_2\, dp_3 = m_0^3 \beta^5\, d\dot{q}_1\, d\dot{q}_2\, d\dot{q}_3.$$

It will be seen that the factor, β^5, arises quite naturally—it is the price we pay for the use of the velocity diagram. The surfaces of equal energy in both diagrams are spheres, the radii being connected by the equation

$$R^2 = m_0^2 \beta^2 \rho^2.$$

The surface corresponding to an infinite energy in one diagram is the sphere at infinity ; in the other the sphere of radius c.

Since the correcting factor is β^5, it appears that $\bar{\epsilon} \to RT$ as $T \to \infty$, *i. e.*, the mean energy tends to exactly double the classical value, as the temperature tends to infinity. The exact formula for ϵ was given in my previous communication.

* We can ignore the coordinates q_1, q_2, q_3, as the energy is assumed not to depend on these coordinates.

LXVII. *Theory of the Internal Action of Thermionic Systems at Moderately High Frequencies.*—Part I.

By W. E. Benham, *B.Sc.**

Abstract.

Equations are given applying to a parallel plane thermionic system subject to potentials varying in time. These equations are similar to Child's equations for steady potentials, but contain extra terms. A solution of the alternating case is obtained, taking into account space-charge but neglecting emission velocities, in the special case of a small oscillatory potential superimposed on a large steady potential. The time of transit of the electrons appears in the solution. The theory is used to explain certain experimental results on the frequency variation of rectified current (W. E. Benham, Phil. Mag., Feb. 28.).

The qualitative agreement between theory and experiment is satisfactory, but the observed effect is much the greater. The discrepancies between theory and experiment are discussed at some length. It is pointed out that electrons emitted with certain velocities are liable to execute a to-and-fro motion about the surface of minimum potential. This effect would increase with the frequency, with a corresponding modification of rectified current.

Introduction.

In a recent paper † experiments were quoted indicating a discrepancy between the static and dynamic characteristic of a diode at moderately high frequencies. In particular, a small oscillatory potential of given amplitude was found to give rise to less and less rectified current as the frequency was increased from 4 to 17 megacycles. Part I. of the present paper constitutes an attempt to explain this phenomenon by taking into account the laws governing the motion of the space-charge when subject to rapidly alternating potential differences. While the theory has only been worked out in the case of zero initial velocities and plane electrodes, it forms nevertheless a possible starting-point for more exact theoretical investigation.

* Communicated by Dr. Norman Campbell.

† W. E. Benham, Phil. Mag. v. p. 323.

Theory.

The now familiar equations of Child *, *e.g.*

$$\frac{d^2V}{dx^2} = -4\pi P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$I = PU, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$U\frac{dU}{dx} = -\frac{e}{m}\frac{dV}{dx}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

are intended to apply only in the case of steady potentials. Any solution of these equations in the form $I=f(V)$ is therefore valid only when I and V are invariant in time. The justification for the standard practice of using the static characteristic, $I=f(V)$, to predict a periodic change in I consequent on a periodic change in V lies in the fact that the response of the electrons can for most practical purposes be taken as instantaneous. When the periodicity of V is very great, however, this is no longer the case. Under these circumstances Child's equations must be extended so that they apply to the case of potentials varying in time.

We shall reserve the symbols V, P, I, and U for the "steady" values of potential, space-charge per unit volume, current density, and velocity.

Let **V**, **P**, **J**, and **U** (in Clarendon type) be the values of potential, space-charge per unit volume, current density, and velocity at any point $(x, 0, 0)$ and instant t. For the present, **V**, **P**, **J**, and **U** may vary with time in any manner.

For moving fields or fields varying with time at a given place, we have

$$\nabla^2\mathbf{V} - \frac{1}{c^2}\frac{\partial^2\mathbf{V}}{\partial t^2} = -4\pi\mathbf{P}.$$

The term $\frac{1}{c^2}\frac{\partial^2\mathbf{V}}{\partial t^2}$ reminds us that the potential is propagated with a finite velocity c. Now, this term can be neglected, provided the (time)^2 taken by e.m. waves to travel a given distance in the region considered is negligible compared not only with the (time)^2 taken by electrons to travel that distance, but also with the (time period of oscillation)^2 of **V**. The first condition is satisfied for fields not exceeding a few thousand volts per cm., while the second is satisfied in the case of periodicities not exceeding some 10^9 cycles per second (for plates 0·5 cm. apart). The conditions for the

* Phys. Rev. xxxii. p. 499 (1911). Used equations for case of positive thermions. For electrons see Langmuir, *loc. cit.* ii. p. 456 (1913).

neglection of the term

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{V}}{\partial t^2}$$

are therefore satisfied experimentally. Since the lines of force are parallel to the axis of x, as for the steady case, we have therefore

$$\frac{\partial^2 \mathbf{V}}{\partial x^2} = -4\pi \mathbf{P}. \quad . \quad . \quad . \quad . \quad . \quad (1\,a)$$

The current density is composed of two parts:

$$\mathbf{J} = \mathbf{PU} - \frac{\partial^2 \mathbf{V}}{\partial x \partial t} \text{ (e.s. units).} \quad . \quad . \quad . \quad (2\,b)$$

The second term represents the displacement, or "capacity" current, while the current **I** actually carried by the thermions is given by

$$\mathbf{I} = \mathbf{PU}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,a)$$

Equating the rate of change of momentum of an electron to the instantaneous value of the electric force acting on it,

$$m\frac{d\mathbf{U}}{dt} = -e\frac{\partial \mathbf{V}}{\partial x}$$

or

$$\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U}\frac{\partial \mathbf{U}}{\partial x} = -\frac{e}{m}\frac{\partial \mathbf{V}}{\partial x}. \quad . \quad . \quad . \quad . \quad (3\,a)$$

Since the current density must be the same at all values of x,

$$\frac{\partial \mathbf{J}}{\partial x} = 0,$$

which leads, with the help of $(2\,b)$ and $(1\,a)$, to

$$\frac{\partial}{\partial x}(\mathbf{PU}) = -\frac{\partial \mathbf{P}}{\partial t}. \quad . \quad . \quad . \quad . \quad . \quad (3\,b)$$

Equations $(3\,a)$ and $(3\,b)$ correspond respectively to the general hydrodynamical equations of motion and continuity. Equation $(3\,b)$ could, of course, have been obtained independently on the basis of analogy with fluids. Writing $\mathbf{I} = \mathbf{PU}$, we have

$$\frac{\partial \mathbf{I}}{\partial x} = -\frac{\partial \mathbf{P}}{\partial t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4\,a)$$

For steady currents it is always true that

$$\frac{d\mathrm{I}}{dx}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (4 *a*) involves that the x-variation of the current carried by the thermions is not in general zero, but is equal and opposite to the x-variation of displacement current.

The equations (1 *a*), (2 *a*), (3 *a*), and (4 *a*) replace (1), (2), (3), and (4) in the case of potentials varying with time not more rapidly than would justify the omission of the term $\frac{1}{c^2}\frac{\partial^2 \mathrm{V}}{\partial t^2}$ from equation (1 *a*). Before proceeding to the solution of equations (1 *a*) to (4 *a*) we note that equations (1) to (4) can be readily solved by the following method.

Differentiating (3) with respect to x and using (1),

$$\frac{d}{dx}\left(\mathrm{U}\frac{d\mathrm{U}}{dx}\right)=4\pi\frac{e}{m}\mathrm{P}.$$

Multiplying throughout by U and using (2),

$$\mathrm{U}\frac{d}{dx}\left(\mathrm{U}\frac{d\mathrm{U}}{dx}\right)=4\pi\frac{e}{m}\mathrm{I}. \quad . \quad . \quad . \quad . \quad (5)$$

In view of (4), I is independent of x.

The solution to (5), subject to $\mathrm{U}=0$ when $x=0$, is

$$\left.\begin{array}{ll} & \text{(i.)} \quad \mathrm{U}=\alpha x^{2/3}, \\ \text{where} & \text{(ii.)} \quad \alpha=\left(18\frac{e}{m}\pi\mathrm{I}\right)^{1/3}. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The well-known 3/2 power law connecting I and V is readily obtained from (6), using (3).

No attempt will be made to include the effect of initial velocities in obtaining a solution to equations (1 *a*) to (4 *a*): the complexity of the solution of the steady case, allowing for initial velocities *, is such as to make an attempt at accurate solution of the alternating case almost out of the question. The undoubtedly important effect of initial velocities is, however, examined qualitatively after a solution for zero emitted velocities has been arrived at. Any solution we obtain will therefore reduce to the form (6), or to expressions obtainable from (6), in the case when the time variation is nil.

* *Cf.* Fry, Phys. Rev. xvii. p. 441 (1921).

Rewriting the equations, for convenience,

$$\frac{\partial^2 \mathbf{V}}{\partial x^2} = -4\pi \mathbf{P}. \quad . \quad . \quad . \quad . \quad . \quad (1\,a)$$

$$\mathbf{I} = \mathbf{P}\mathbf{U}. \quad . \quad . \quad . \quad . \quad . \quad (2\,a)$$

$$\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U}\frac{\partial \mathbf{U}}{\partial x} = -\frac{e}{m}\frac{\partial \mathbf{V}}{\partial x}. \quad . \quad . \quad . \quad . \quad (3\,a)$$

$$\frac{\partial \mathbf{I}}{\partial x} = -\frac{\partial \mathbf{P}}{\partial t}. \quad . \quad . \quad . \quad . \quad (4\,a)$$

Differentiating $(3\,a)$ with respect to x, and using $(1\,a)$,

$$\frac{\partial}{\partial x}\left(\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U}\frac{\partial \mathbf{U}}{\partial x}\right) = 4\pi\frac{e}{m}\mathbf{P}.$$

$$\therefore \qquad \mathbf{U}\frac{\partial}{\partial x}\left(\frac{\partial \mathbf{U}}{\partial t} + \mathbf{U}\frac{\partial \mathbf{U}}{\partial x}\right) = 4\pi\frac{e}{m}\mathbf{I}. \quad . \quad . \quad . \quad (7)$$

Integrating equation $(4\,a)$ at constant t for the space between the cathode and any place $x = x$,

$$\mathbf{I} - \mathbf{I}_0 = -\frac{\partial}{\partial t}\int_{x=0}^{x=x} \mathbf{P}\,dx$$

$$= \frac{1}{4\pi}\frac{\partial}{\partial t}\left|\frac{\partial \mathbf{V}}{\partial x}\right|_0^x.$$

Now, from (6) and (3),

$$\frac{d\mathbf{V}}{dx} = \mathbf{U}\frac{d\mathbf{U}}{dx} = \frac{2}{3}\alpha^2 x^{1/3};$$

i. e., $$\left|\frac{d\mathbf{V}}{dx}\right|_0 = 0.$$

We shall assume that at all instants $\mathbf{V}$ differs so little from V that, as in the steady case, the field at the cathode is at all instants vanishingly small compared with its value at the plane $x = x$, up to which we have integrated. It should be noted that, even in the steady case, it is necessary to suppose that $\left|\frac{d\mathbf{V}}{dx}\right|_0$, while differing from zero by as small a quantity as we please, is always positive, otherwise no electrons starting from rest would be extracted from the cathode. In the present case, also, we must suppose that $\left|\frac{\partial \mathbf{V}}{\partial x}\right|_0$ is never actually negative at any instant. The sequel is thus confined to the case of a very small variable potential

superimposed on a large steady potential. Omitting the term $\left|\frac{\partial \mathrm{V}}{\partial x}\right|_0$,

$$\frac{1}{4\pi}\frac{\partial}{\partial t}\left(\frac{\partial \mathrm{V}}{\partial x}\right) = \mathrm{I} - \mathrm{I}_0$$

or
$$\frac{\partial}{\partial t}\left(\mathrm{U}\frac{\partial \mathrm{U}}{\partial x} + \frac{\partial \mathrm{U}}{\partial t}\right) = 4\pi\frac{e}{m}(\mathrm{I}_0 - \mathrm{I}). \quad . \quad . \quad . \quad (8)$$

Adding equations (7) and (8), thus eliminating I,

$$\left(\frac{\partial}{\partial t} + \mathrm{U}\frac{\partial}{\partial x}\right)\left(\frac{\partial \mathrm{U}}{\partial t} + \mathrm{U}\frac{\partial \mathrm{U}}{\partial x}\right) = 4\pi\frac{e}{m}\mathrm{I}_0. \quad . \quad . \quad (5\,a)$$

Equation (5 *a*) is to be compared with equation (5) for the "steady" case. Now we can make I_0 what we please, as it is a boundary value of current. Let

$$\mathrm{I}_0 = \mathrm{I}_0 + \hat{i}_0 \sin pt + \hat{i}_0' \sin^2 pt + \ldots, \quad . \quad . \quad . \quad (9)$$

where I_0, $\hat{i}_0$, $\hat{i}_0'$ are independent of t. We are not immediately concerned with the values of $\hat{i}_0$, $\hat{i}_0'$ beyond asserting that they are respectively of the first and second order of small quantities. Accordingly let

$$\mathrm{U} = \mathrm{U} + u + u' + \ldots, \quad . \quad . \quad . \quad . \quad (10)$$

where U is defined as obeying the relation

$$\mathrm{U}\frac{d}{dx}\left(\mathrm{U}\frac{d\mathrm{U}}{dx}\right) = 4\pi\frac{e}{m}\mathrm{I}_0, \quad . \quad . \quad . \quad . \quad (11)$$

while u, u' ... must be chosen to satisfy the partial differential equation (5 *a*) with the help of (9), (10), and (11). Since I_0 is independent of t, so also must U be ;

i. e.,
$$\frac{\partial \mathrm{U}}{\partial t} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

With the help of (9), (10), (11), and (12), (5 *a*) gives rise to an equation which may be split into three equations, corresponding to the three terms of equation (9).

The first is equation (11) itself ; the second is linear in u and $\hat{i}_0$ and does not contain u' and $\hat{i}_0'$; while the third is linear in u' and $\hat{i}_0'$, and of the second degree in u and $\hat{i}_0$. There will, of course, be as many equations as there are terms in equation (9), but since we are taking $\hat{i}_0'$ and u' to be of the second order of small quantities, it is sufficient to retain

three only. The second equation reads:

$$U\frac{\partial}{\partial x}\left(u\frac{\partial U}{\partial x}+U\frac{\partial u}{\partial x}\right)+u\frac{\partial}{\partial x}\left(U\frac{\partial U}{\partial x}\right)+\frac{\partial^2 u}{\partial t^2}$$
$$+\frac{\partial}{\partial t}\left(2U\frac{\partial u}{\partial x}+u\frac{\partial U}{\partial x}\right)=4\pi\frac{e}{m}\hat{i}_0\sin pt. \quad (13)$$

The third reads:

$$U\frac{\partial}{\partial x}\left(u'\frac{\partial U}{\partial x}+U\frac{\partial u'}{\partial x}\right)+u'\frac{\partial}{\partial x}\left(U\frac{\partial U}{\partial x}\right)$$
$$+\frac{\partial^2 u'}{\partial t^2}+\frac{\partial}{\partial t}\left(2U\frac{\partial u'}{\partial x}+u'\frac{\partial U}{\partial x}\right)$$
$$+U\frac{\partial}{\partial x}\left(u\frac{\partial u}{\partial x}\right)+u\frac{\partial}{\partial x}\left(u\frac{\partial U}{\partial x}+U\frac{\partial u}{\partial x}\right)$$
$$+2\frac{\partial}{\partial t}\left(u\frac{\partial u}{\partial x}\right)=4\pi\frac{e}{m}\hat{i}_0'\sin^2 pt. \quad . \quad . \quad (14)$$

In order to obtain a solution to equation (13), we must use the solution of (11), which is evidently

$$U=\alpha x^{2/3}. \quad Cf. (6).$$

It is convenient to effect the transformations

$$\left.\begin{aligned}\frac{3}{\alpha}\cdot px^{1/3}&=\xi,\\ u&=\frac{\omega}{\xi}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and the substitutions

$$\left.\begin{aligned}\gamma&\equiv\frac{3}{\alpha},\\ \beta&\equiv 4\pi\frac{e}{m}\hat{i}_0.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Then

$$\left.\begin{aligned}U&=\frac{3\xi^2}{\gamma^3 p^2},\\ \frac{\partial}{\partial x}&=\frac{\gamma^3 p^3}{3\xi^2}\frac{\partial}{\partial\xi},\\ U\frac{\partial}{\partial x}&=p\frac{\partial}{\partial\xi},\\ \frac{\partial U}{\partial x}&=2\frac{p}{\xi}.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Equation (13) then becomes

$$\frac{\partial^2\omega}{\partial\xi^2}+\frac{2}{p}\frac{\partial}{\partial t}\frac{\partial\omega}{\partial\xi}+\frac{1}{p^2}\frac{\partial^2\omega}{\partial t^2}=\frac{\beta}{p^2}\xi\sin pt,$$

or, symbolically,

$$\left(\frac{\partial}{\partial\xi}+\frac{1}{p}\frac{\partial}{\partial t}\right)^2\omega=\frac{\beta}{p^2}\xi\sin pt. \quad . \quad . \quad . \quad (18)$$

Equation (18) can be solved in two stages, and the result is, putting $\omega=u\xi$,

$$u=-\frac{\beta}{p^2}\left(\sin pt+\frac{2\cos pt}{\xi}\right)+\frac{1}{\xi}\mathrm{F}_1(\xi-pt)+\mathrm{F}_2(\xi-pt), \quad (19)$$

where F_1, F_2 are arbitrary functions.

Since $u=0$ when $x=0$, *i. e.* when $\xi=0$, for all values of t the functions F_1, F_2 must be chosen accordingly. The solution can then be written in any of the following forms :—

$$\left.\begin{aligned} u&=-\frac{\beta}{p^2}\left[\sin pt+\frac{2}{\xi}\cos pt+\sin(pt-\xi)-\frac{2}{\xi}\cos(pt-\xi)\right],\\ u&=+\frac{\beta}{p^2}\left[\left(-\cos\xi+\frac{2}{\xi}\sin\xi-1\right)\sin pt\right.\\ &\qquad\left.+\left(\sin\xi+\frac{2}{\xi}\cos\xi-\frac{2}{\xi}\right)\cos pt\right],\\ \frac{u}{\mathrm{U}}&=\frac{\hat{i}_0}{3\mathrm{I}}\Upsilon_u\sin(pt-\Xi_u).\end{aligned}\right\} \quad . \quad . \quad . \quad (20)$$

N.B.—It will be found on substitution that $\frac{\beta\xi^2}{6p^2}=\frac{\hat{i}_0\mathrm{U}}{3\mathrm{I}}$.

The last form serves to demonstrate the effect of frequency on the value of u at any point. We have

$$\left.\begin{aligned}\Upsilon_u&=\frac{12}{\xi^2}\left[\frac{\sin\frac{1}{2}\xi}{\frac{1}{2}\xi}-\cos\tfrac{1}{2}\xi\right],\\ \Xi_u&=\tfrac{1}{2}\xi.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (21)$$

Whence, as $\xi\to0$, $\Upsilon_u\to1$ and $\Xi_u\to0$.

Before proceeding with the solution, we would draw attention to the physical meaning of ξ.

In total differential notation

$$\mathrm{U}=\frac{dx}{dt}.$$

$$\therefore \quad dt = \frac{dx}{U}$$

$$= \frac{d\xi}{p} \text{ by equation (17).}$$

$$\therefore \quad \xi = pT, \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad (22)$$

where T = time of transit of electrons from cathode to plane in question in the absence of alternating current. We note in passing one consequence of this result.

For $pT = 2\pi$,

$$\Upsilon_u = \frac{3}{\pi^2}, \quad \Xi_u = \pi.$$

Hence, when the time period of oscillation is equal to the time of transit, the amplitude of motion at the plane in question is reduced some 70 per cent. as a direct result of the extreme rapidity of alternation, the reduction in amplitude being accompanied by a reversal of phase at this plane.

The above result may be useful in connexion with the oscillations of extremely short wave-length discovered by Barkhausen and Kurz *, whose experiments were repeated in this country by Gill and Morell †. This point will, however, be deferred to Part II. of this paper.

Having obtained U and u, we are now in a position to solve equation (14) for u'. The mathematics are greatly simplified if we content ourselves with an approximate formula for u in which $\left.\begin{matrix}\cos\\ \sin\end{matrix}\right\}\xi$ have been replaced by their appropriate expansions in powers of ξ; *e. g.*,

$$\frac{\beta\xi^2}{6p^2}\left[\left(1 - \frac{3\xi^2}{20} + \frac{\xi^4}{161} - \ldots\right)\sin pt - \left(\frac{\xi}{2} - \frac{\xi^3}{30} + \ldots\right)\cos pt\right].$$

. . . (23)

The above expression differs by much less than 1 per cent. from the exact formula, for $0 < \xi < 2$. The details of analysis need not be entered into. The solution is naturally of the general form

$$u' = X + Y \sin 2pt + Z \cos 2pt. \quad . \quad . \quad . \quad (24)$$

The values of Y and Z are not of immediate interest, and need not be written down. The mean value of u' during the cycle is as follows:

$$\bar{u}' = X = \frac{U}{18I}\left[3\hat{i}_0' - \frac{\hat{i}_0^2}{I}\left(1 - \frac{\xi^2}{16} + \frac{11\xi^4}{8400}\right)\right] . \quad (25)$$

* *Phys. Zeit.* xxi. p. 1 (1920).

† Phil. Mag. xliv. p. 161 (1922).

We have now completely determined $\mathbf{U}$ in terms of I_0, $\hat{i}_0$, and $\hat{i}_0'$. We can now substitute for $\mathbf{U}$ in equation $(3a)$ to obtain $\mathbf{V}$ in terms I_0, $\hat{i}_0$, and $\hat{i}_0'$. For this purpose let

$$\mathbf{V} = V + v + v'. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The values of V, v/V are found to be as follows:

$$\left.\begin{aligned} V &= \left(\frac{I_0}{k}\right)^{2/3} . x^{4/3}, \\ \text{in which} \qquad k &= \sqrt{\left(\frac{2e}{m}\right)}\Big/ 9\pi, \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad (27)$$

$$\frac{v}{V} = \left(\frac{2\hat{i}_0}{3I_0}\right)\Upsilon_v \sin(pt - \Xi_v), \quad . \quad . \quad . \quad (28)$$

where, for $0 < \xi < 2$,

$$\left.\begin{aligned} \Upsilon_v^2 &= 1 - \frac{13\xi^2}{300} + \frac{11\xi^4}{12{,}600}, \\ \Xi_v &= \frac{3\xi}{10}. \end{aligned}\right\} . \quad . \quad . \quad . \quad (29)$$

If $\bar{v}'$ denote the mean value v' during the cycle, we find also

$$\frac{\bar{v}'}{V} = \left(\frac{1}{18I_0}\right)\left[6\hat{i}_0' - \frac{\hat{i}_0^2}{I_0}\left(1 - \frac{3\xi^2}{40} + \frac{13\xi^4}{8400}\right)\right] . \quad . \quad (30)$$

Now, *at the anode*, $\bar{v}'$ must vanish, since the anode is maintained at a potential V with respect to the cathode by means of a battery. In actual practice the potential at the anode is to some extent modified by any resistance in the anode circuit, but when such resistance is negligible compared with that of the valve, the mean potential of the anode can be taken as the battery potential. These conditions were actually realized in the experiments, since the battery was of the accumulator type having low internal resistance, the only other resistance being that of the shunted galvanometer arrangement, which was also negligible.

Hence, *at the anode*, for all frequencies

$$\bar{v}' = 0,$$

whence from (30):

$$\frac{\hat{i}_0'}{2} = \frac{\hat{i}_0^2}{12I_0}\left(1 - \frac{3\xi_d^2}{40} + \frac{13\xi_d^4}{8400}\right) . \quad . \quad . \quad . \quad (31)$$

The suffix "d" denotes that the value of ξ is that corresponding to the anode $(x = d)$. Equation (31) gives the

rectified current $\hat{i}_0'/2$ in terms of $\hat{i}_0$ and ξ_d. It must be emphasized that, while the *rectified* current varies with ξ_d (*i. e.* with p), it by no means varies with ξ (*i. e.* with x), as does the alternating component of *thermionic* current (*q.v.*). For the cathode-anode space we have, from (30) and (31),

$$\frac{\bar{v}'}{V} = \frac{i_0^2}{18 I_0}\left[\frac{3}{40}\cdot(\xi^2-\xi_d^2) - \frac{13}{8400}\cdot(\xi^4-\xi_d^4)\right]. \quad (32)$$

Since $\xi \leq \xi_d$, we draw the following conclusion for future reference; *e.g.* :—

"*For given boundary values of the potential components, the mean potential at any point intermediate between cathode and anode is less at finite frequencies than at zero frequency.*"

We have yet to express the rectified current in terms of the boundary value of the alternating component of *potential*. Let $\hat{v}$ denote the amplitude of v. Then, from equation (28),

$$\frac{\hat{v}}{V} = \left(\frac{2\hat{i}_0}{3 I_0}\right)\Upsilon_v.$$

Hence (31) becomes, substituting for $\hat{i}_0$,

$$\frac{\hat{i}'}{2} = \left(\frac{3 I_0}{16}\right)\left(\frac{\hat{v}^2}{V^2}\right)\left(\frac{1}{\Upsilon_v^2}\right)\left(1 - \frac{3\xi_d^2}{40} + \ldots\right).$$

Substituting for Υ_v^2 from (29) and putting $\xi = \xi_d$, $v = v_d$, $V = V_d$, we have, after rationalising,

$$\frac{\hat{i}_0'}{2} = \left(\frac{3 I_0}{16}\right)\left(\frac{\hat{v}_d^2}{V_d^2}\right)\left(1 - \frac{19\xi_d^2}{600} - \frac{7\xi_d^4}{10{,}000}\right),$$

in which little accuracy is claimed for the last term, which is, fortunately, exceedingly small.

Thus, for given values of $\hat{v}_d$ and V_d the rectified current varies with the frequency according to the expression in round brackets. We shall refer to this expression for convenience as $\Upsilon_{\Delta I}$.

In decimal form we have

$$\Upsilon_{\Delta I} = (1 - 0{\cdot}0317\,\xi_d^2 - 0{\cdot}0007\,\xi_d^4). \quad . \quad . \quad (33)$$

Application to Experimental Results.

$\Upsilon_{\Delta I}$ has been plotted on fig. 1 for values of ξ between 0 and 3. We note a general agreement in form between theoretical and experimental curves.

For plates 0·5 cm. apart subject to an anode potential of 16 volts we find, after expressing ξ_d in terms of p, V, and d

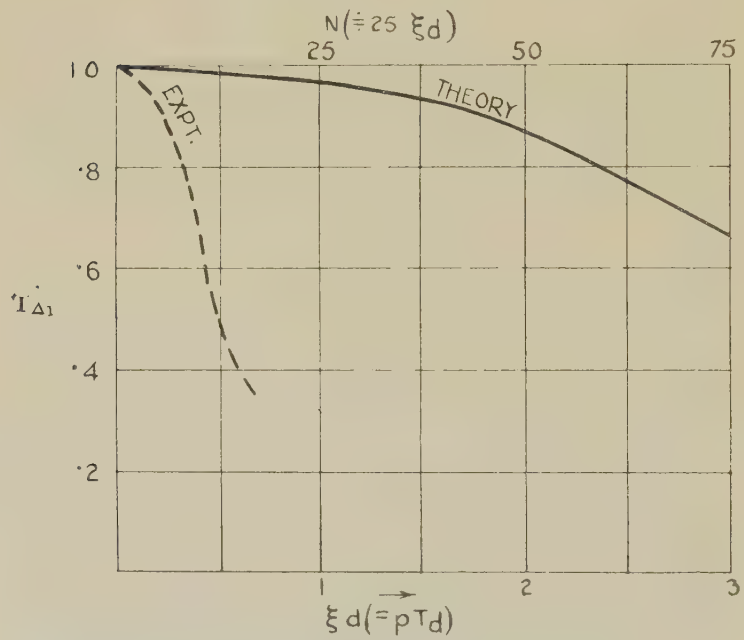
($q.v.$ equation 36), that the frequency in megacycles (1 megacycle $=10^6$ cycles/sec.) is given very nearly by

$$N=25\xi.$$

Thus for a frequency of 12·5 megacycles ($\lambda 24m$), which corresponds to a typical frequency in the range of experiments,

$$\xi=0{\cdot}5.$$

Fig. 1.



Variation of Rectified Current with Frequency.
(N=frequency in megacycles.)

So that in this case

$$\Upsilon_{\Delta I}=1-0{\cdot}0072=0{\cdot}992. \quad . \quad . \quad . \quad . \quad (34)$$

According to the experimental curves, however, we have, at N 12·5,

$$\Upsilon_{\Delta I}\doteqdot 0{\cdot}5. \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The frequency variation obtained in practice is therefore very much more pronounced than that predicted by equation (33). In order to bring the experimental curves into approximate agreement with the formula (33), it would be

necessary to assume that the time of transit of the electrons were about five times the time of transit calculated from the formula

$$T_d = \frac{3d}{\sqrt{\left(2 \cdot \frac{-e}{m} \cdot V\right)}} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Moreover (36) refers to parallel planes ; for cylinders it can be shown that for the same clearance and potential difference the time of transit approaches $T_d/2$ as the radius of the cathode approaches zero. The effective anode radius corresponding to the valves used would be intermediate between the radii of grid and anode (these electrodes, being connected external to the valve, are both at the same time potential). The effective anode radius, while somewhat indeterminate, cannot differ much from 0·5 cm.

Thus to obtain any sort of quantitative agreement with equation (33) it would be necessary to assume that, due to some cause, the actual time of transit of the electrons were about ten times the time of transit calculated directly from the dimensions and potentials.

Other Factors influencing the Time of Transit.

Increase in the average time of transit would result :

(*a*) If some of the electrons were to suffer collisions with molecules before completing transit.

(*b*) If the result of such collisions were to produce ionization ; *i. e.*, to give rise to heavy thermions.

(*c*) From consideration of finite emission velocities.

In view of the high vacuum ($\pi \gg 10^{-5}$ mm. Hg), it is safe to conclude that the effects (*a*) and (*b*), while inevitably present if only in a minute degree in every thermionic device, are not responsible for more than a small fraction of the increase in time of transit. These remarks are not intended to apply to any of the results quoted for a helium-filled valve. The effect of (*c*) will be examined when we have inquired into other possible experimental factors tending to increase the frequency variation.

One such possibility is that the e.m.f. measured by the electrometer was not composed exclusively of the fundamental component v, but partly of harmonic components.

The Effect of Harmonics in the Oscillatory Voltage.

It is convenient to divide voltage harmonics into two kinds:—

(1) Those produced from the fundamental by the valve itself in virtue of its peculiar conducting properties.

(2) Those introduced along with the fundamental from the source of oscillations.

Both types of harmonics are registered by the electrometer in addition to the fundamental. Thus, if harmonics in the voltage, whether of type (1) or (2), are comparable in amplitude to the fundamental, the electrometer reading will be greater than that corresponding to the mean square of v; *i. e.*, greater than that corresponding to the rectified current. The harmonics in the current will increase as the harmonics in the potential increase, but the important point to notice is that current harmonics are not registered, while potential harmonics are. The rectified current is clearly due only to the fundamental v over the range of v for which square law rectification takes place.

We have therefore to inquire into the effect of potential harmonics of both types on the electrometer reading.

In order to find the magnitude of type (1) harmonics, it is necessary to work out the values of Y and Z (equation 24) and then to use equation $(3\,a)$ to find the corresponding potential harmonics. The mathematics involved is exceedingly clumsy, and it will suffice to give the final approximate result, which is correct to 5 per cent. for $0<\xi<0{\cdot}5$; namely

$$v'=0{\cdot}375\,\frac{\hat{v}^2}{\Upsilon_v\mathrm{V}}\,(0{\cdot}128\,\xi\sin 2pt-0{\cdot}136\,\xi^2\cos 2pt). \quad (37)$$

That the value of v' at finite frequencies is not zero involves that it is impossible to avoid potential harmonics, even though the potential wave-form be pure in the absence of the thermionic device. It turns out, however, that v' is exceedingly small at practical frequencies (at any rate for a system obeying the 3/2 power law). The electrometer reading is proportional to

$$\int_{t=0}^{t=p/2\pi}(v+v')^2\,dt,$$

which gives finally

$$\frac{\hat{v}^2}{2}\left(1+0{\cdot}00015\,\frac{\hat{v}^2}{\mathrm{V}^2}\,\xi^2\right).$$

The effect of harmonics of type (1) is thus exceedingly small and can be neglected.

Harmonics of type (2) must next be considered. These are much easier to deal with. Thus instead of considering the fundamental, which we will call v_1, as the input oscillatory voltage, one might equally well consider the harmonic v_n to be the input oscillatory voltage. The rectified current due to v_n will then be proportional to

$$\hat{v}_n^2[1-0{\cdot}0317(n\xi)^2-\ldots], \quad . \quad . \quad . \quad (38)$$

in which n is the order of the harmonic and ξ still corresponds to the fundamental frequency.

The rectified current due to the fundamental and $n-1$ harmonics of type (2) is thus proportional to the sum to n terms of the above expression.

It is therefore necessary to know the relative amplitudes of any harmonics in the input, or preferably to cut them out altogether—if possible. One method of cutting out the harmonics which is fairly effective is to couple a tuned circuit loosely to the oscillator coil, and then couple the valve test circuit to this tuned circuit. This was done, but the frequency variation proved to be the same within experimental error.

It appears, therefore, that both kinds of harmonics in the input voltage were of amplitude negligible compared with that of the fundamental; and we conclude that the observed frequency variation was that corresponding to the fundamental frequency alone.

The large discrepancy between theoretical and observed frequency variation is thus left unexplained by the foregoing considerations. The time is now ripe for noting a further important discrepancy between theory and experiment. It was found that change in the anode voltage had negligible effect on the frequency variation over a range of voltages corresponding to the infra-saturation region: change of anode voltage, of course, alters the absolute value of the rectified current, but the ratio of the rectified current at any two frequencies was found to be sensibly independent of the anode voltage. But in view of the dependence of the calculated time of transit T on anode voltage, any frequency variation due to the finite value of T must become less pronounced as the anode voltage is increased. Hence the frequency variation due to the finite time of transit T must be too small to affect the observations.

In order to account for the observations, it is accordingly necessary to suppose that the actual *effective* time of transit in sensibly independent of V and considerably greater

than T. We therefore put forward the following tentative suggestions as working hypotheses :—

(1) The electrons take a finite average time T_f to free themselves from the neighbourhood of the filament, T_f being sensibly independent of V and considerably greater than T.

(2) T_f is determined by the condition of the filament, especially by the filament temperature.

The second hypothesis seems a reasonable adjunct to the first, and is in qualitative agreement with the observed marked effect of filament voltage on the frequency variation.

We will now examine the effect of initial velocities, with the above hypotheses in mind.

The theory for zero initial velocities is at best only an approximation to the actual facts. The behaviour of the electrons in the neighbourhood of the filament is, in fact, totally different from the case of zero emitted velocities *.

The theory for zero initial velocities applies, strictly speaking, only in cases in which the accelerating field due to the anode potential everywhere exceeds the retarding field due to the space-charge, the excess vanishing, however, at the filament $\left(\frac{dV}{dx} \to 0, \text{ when } x \to 0\right)$. It is noteworthy that, in order to drag the (hypothetically at rest) electrons away from the filament, it must be supposed that $\left|\frac{dV}{dx}\right|_0$ is slightly positive, but can be made, for the purposes of the theory for zero emitted velocities, to differ from zero by an infinitesimal amount. Thus, in the theory for zero emitted velocities,

$$\left|\frac{dV}{dx}\right|_0 \to \delta \to 0.$$

Furthermore, if δ is positive, *all* the emitted electrons will reach the anode: if negative, *none* †.

* *Cf.* Fry (*loc. cit.*) and Langmuir, Phys. Rev. xxi. p. 419 (1923).

† That the 3/2 power law is a sufficiently accurate relation for many practical purposes is at first sight somewhat surprising. The widespread practical application of the 3/2 power law, especially in the design of large valves, is justified by the closeness of the cathode to the surface of minimum potential, which surface may be regarded as a "virtual cathode" at which $\left(\frac{dV}{dx}\right)_0 = 0$. This does not alter the fact that the

Now, in the practical case of finite emission velocities δ is negative in the infra-saturation region, since all the electrons do not reach the anode. For δ negative there will be a surface of minimum potential $\left(\left|\frac{dV}{dx}\right|_1 = 0\right)$ at some value x_1 of x. If U_c be the critical value of initial velocity, such that electrons emitted with this velocity come to rest at $x = x_1$, the time of transit of these electrons to the anode (assuming the electrons just to *succeed* in passing the plane $x = x_1$) is greater than the time of transit for $x_1 = 0$, $U_0 = 0$. This point is illustrated *, for $x_1 = 1$ mm., $d = 5$ mm., on fig. 2. The ordinates to these curves represent, in arbitrary units, the time of transit to any abscissa x. The value of T corresponding to $U_0 = V_c$ is taken to be proportional to $[(x - x_1)^{1/3} + x_1^{1/3}]$, since it follows from equation (5) that, for those electrons which come to rest at $x = x_1$,

$$U = \alpha(x - x_1)^{2/3};$$

$$i.e., \quad U_c = \alpha(-x_1)^{2/3} = +\alpha x_1^{2/3}.$$

Curves corresponding to U_0 slightly less and slightly greater than U_c are clearly indicated on fig. 2.

A slight disturbance in potential at the instant when the electron reaches the potential minimum suffices to determine whether it will return to the filament or whether it will pass over to the anode. In the event of the disturbance being of oscillatory character, the electrons which are momentarily at rest, or nearly so, will be made to execute a to-and-fro motion of small amplitude † about the surface of minimum potential. Perhaps it would be more accurate to say that the surface of minimum potential executes a to-and-fro motion about the electrons, placing the latter first in an accelerating and then in a retarding field. It is

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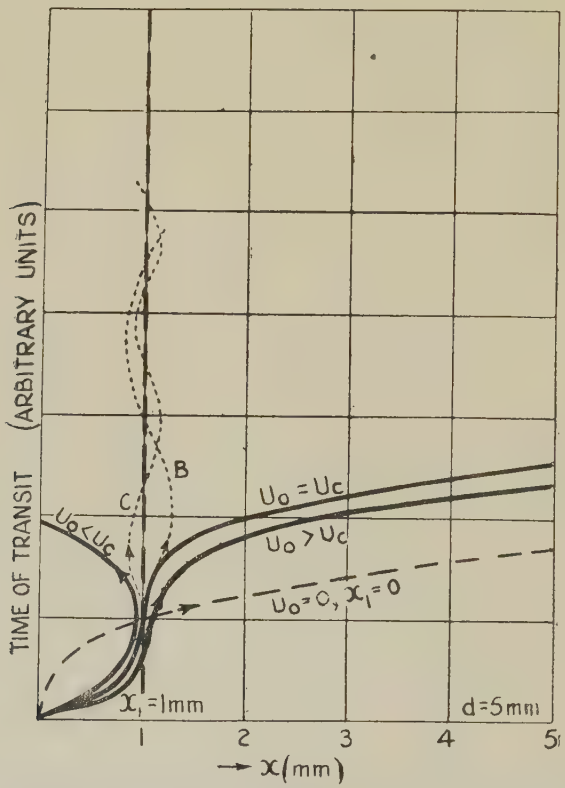
field at the actual cathode is, in general, very different from zero, whether or no the 3/2 power law gives accurate results. At the surface of minimum potential the mean velocity of the electrons is, of course, very much less than at the cathode. Thus at the "virtual cathode" the condition of zero "emission" velocity is approached, and the condition of zero field is realized.

* For a plane cathode at 2400° K. the anode potential for $x_1 = 1$ mm. $d = 5$ mm. is only 2 v. and only 0·1 per cent. of the emitted electron reach the anode. The example is thus an extreme one.

† *Cf.* Zilitinkewitsch, *Archiv. f. Electrot.* xv. p. 482 (1925), who assumed electrons to oscillate in a somewhat similar manner in the case of a valve generating oscillations of the type discovered by Barkhausen and Kurz (*loc. cit.*).

legitimate to regard the electrons as executing oscillations about the mean position of the potential minimum. The electrons in question will presumably remain indefinitely in this oscillating condition (B, C, fig. 2). For a given frequency, the number of electrons so oscillating is equal to the number of electrons reaching the potential minimum

Fig. 2.



The time taken by electrons emitted with velocities in the neighbourhood of the critical velocity (see text) to reach any plane $x=x$ is illustrated above in the special case $x_1=1$ mm., $d=5$ mm.

with velocities less than a certain small value U_m, where U_m will depend on the amplitude of the applied potential as well as on the cathode temperature. Since U_m can be greater for larger values of $\hat{v}$, the number of oscillating electrons would increase with the value of $\hat{v}$. Clearly, also, U_m can

be greater the greater the frequency (within certain limits), so that the number of oscillating electrons increases with the frequency. Periodical instability at high frequencies is likely, such as was noticed in the experiments ; the observed instabilities were then put down to the Schottky effect.

We can, if we like, regard the effective average time of transit as being lengthened due to certain electrons remaining an indefinite time in the cathode-anode space. But this conception, while exceedingly convenient from the mathematical standpoint, is unsatisfactory from the physical point of view. One physical consequence of electrons oscillating about the potential minimum is an increased space-charge density in that region.

Now, the theory for zero initial velocities gives some indication of accumulated space-charge. The mean potential at any point in the cathode-anode space was found to be less at finite frequencies than at zero frequency (equation 32). This result is closely related in the theory to the frequency variation of the rectified component of current (equation 31). The reason for the reduction in potential is bound up with the peculiar conducting properties of thermionic systems. The interpretation of the reduction follows from the fact that for a given mean anode potential a reduction in mean potential at any point in the cathode-anode space can only be brought about by an increase of space-charge density at that point.

Now, in practice the increase of space-charge density, *i. e.* the reduction in mean potential, especially at points near the potential minimum, is likely to be on a much larger scale than in the theory for initial velocities, in view of accumulated space-charge due to oscillating electrons. If, then, the frequency variation of rectified current is, in fact, as closely related to the increase of space-charge density as it is in theory, the observed frequency variation would, like the reduction in mean potential, be on a much larger scale than that predicted by the theory for zero emitted velocities.

If the true explanation of the observations lies in the direction indicated, the effects of filament and anode voltages on the value of the rectified current are alike somewhat obscure ; a purely physical explanation, if not altogether out of the question, would be very involved.

Such questions could be settled by further experiments on a larger scale and with improved apparatus. The sensitivity of the instrument used to measure the oscillatory voltage should be as great as is consistent with rapidity of

reading: no valve keeps absolutely constant characteristics over a period of an hour, especially under the somewhat severe conditions of experiment, and the smallest changes are of vital importance in measurements of this kind. The idiostatically-connected Dolezalek electrometer is definitely not sufficiently sensitive and the needle takes too long to come to rest.

The electrometer might be disposed of when the frequency variation of one valve has been fully determined, as this valve could then be incorporated in a Moullin voltmeter circuit, whose frequency error would be known. The voltmeter thus provided is very much more convenient to work with. Incidentally, the author's experiments on a helium-filled valve were effected in this manner. The valve used as voltmeter was a Marconi D.E.V. type valve which showed a negligible frequency error when used as triode. In chosing a valve for investigation a simple form of electrode design is desirable. Indirectly heated cathode valves are now available. These valves conform very nearly to the theoretical parallel plane system.

This research was begun early in 1926 at University College, London, under the supervision of Professor A. W. Porter, F.R.S., and with much appreciated financial assistance from the Department of Scientific and Industrial Research.

The author wishes to thank Professor Porter for his able advice and opportune criticism on many occasions, and all those who have taken an interest in the work for helpful suggestions. He would also like to thank Dr. Campbell for his great kindness in communicating the paper.

Summary.

1. With the more immediate object of explaining certain experimental results on frequency variation of rectified current, but also as a starting-point for further theoretical investigation, Child's space-charge equations are modified so as to make them apply to the case of potentials varying in time.

2. The equations of motion and continuity represent the electrical counterpart of the corresponding hydrodynamical equations.

3. The equation of continuity in the thermionic case involves that, while the sum of the instantaneous values of

thermionic and displacement (capacity) current is the same at all points, each type of current varies from point to point.

4. The primary equation (5 *a*) obtained from the modified equations (1 *a*) to (4 *a*) lends itself to solution if we assign a permissible value to the current at the cathode. It is supposed that the alternating components of current and potential are of very small amplitude. The corresponding alternating components of velocity are thus obtained at any value of x and t.

5. These velocity components come out in functions of $\xi\left(=\frac{3}{\alpha}px^{1/3}=p\mathrm{T}\right)$. The interpretation of ξ follows from the fact that T represents the time of transit of electrons from the cathode ($x=0$) to any plane ($x=x$).

6. A solution for the potential is obtained by inserting the solution for the velocity in equation (3 *a*).

7. By imposing on this last solution the experimentally-realised condition that the mean potential difference between cathode and anode is constant (being maintained so by the anode battery), a relation between the rectified current and the alternating component of current is obtained, involving functions of $\xi_d(=p\mathrm{T}_d)$, where T_d is the time of transit from cathode to anode.

8. A further short analysis gives the rectified currents in terms of ξ_d and the potential components.

9. The solution obtained agrees qualitatively with the experimental results, but the magnitude of the frequency variation predicted by theory is much smaller than that found by observation.

10. In order to bring theory and observation into line, it is necessary to suppose that the time of transit is for some reason much greater than the value calculated from the dimensions and potentials of the valve. It is not possible to explain the observed variation of (square-law) rectified current on the basis of harmonics in the potential.

11. It is pointed out that collisions with residual molecules are too infrequent to produce the required lengthening of time of transit.

12. A further discrepancy between theory and practice lies in the apparent non-dependence of frequency variation on (steady) anode potential.

13. To account for the discrepancies the working hypothesis is adopted: "That the electrons take a certain time to escape from the proximity of the filament, this time being

determined by the temperature of the filament, but hardly at all by the anode potential."

14. Due to initial velocities a surface of minimum potential is present for voltages below saturation. Electrons emitted with a certain critical velocity execute oscillations about the surface of minimum potential. Mathematically this effect can be interpreted as giving rise to an increased effective average time of transit.

15. The physical consequence of this effect is accumulated space-charge in the neighbourhood of the potential minimum. A certain result obtained in the theory (equation 32) is used to associate the frequency variation of rectified current with the degree of accumulation of space-charge. Further lines for experiment are suggested.

LXVIII. *The Thermal Instability of the Earth's Crust.* *By* H. H. Poole *Sc.D.*, *and* J. H. J. Poole, *Sc.D.**

IN Dr. Jeffreys's interesting, if rather heated, paper on "Dr. Joly and the Earth's Thermal History" in the January number of the Philosophical Magazine, his main contention seems to be that, if the substratum contains more radioactive elements than are sufficient to supply the present loss of heat from the earth's surface, the future state of the earth will be one in which a layer of molten rock of fixed thickness and temperature-gradient will be overlain by a solid crust, also of a fixed thickness. The thickness of this crust will be such that the loss of heat by conduction through it will exactly counterbalance the generation of radioactive heat, both in itself and in the underlying layers, so that a steady state will be attained with no possibility of any orogenic movements due to thermal expansion or contraction. As, according to Dr. Jeffreys, the earth is about 1300 million years old already, it seems peculiar that it has not yet reached this state. Moreover, if, as he assumes, the earth has always been falling in temperature, we should not expect the present temperature gradient to be less than the finally-attained gradient, which must be sufficient to carry off the heat generated.

The only logical conclusion that can be drawn from this assumption is that the substratum cannot contain more radioactive materials than are sufficient to account for the present rate of loss of heat.

* Communicated by the Authors.

This view is opposed by all the actual measurements of the uranium and thorium contents of the materials which might be reasonably supposed to constitute the substratum ; but, of course, its incorrectness cannot be absolutely proved by experiment, as we are unable to obtain specimens of absolutely unimpeachable derivation from the layer in question.

However, apart entirely from this consideration, his contention is based on the assumption that it would be possible for a layer of molten magma to persist indefinitely beneath a roof of solidified magma of the same composition. A very elementary consideration of the thermodynamical principles involved shows that this assumption cannot be true, unless the magnitude of the subterranean pressures introduces effects which, *a priori*, we would not expect.

It is well known that, as Dr. Jeffreys points out, in a deep layer of liquid, if the vertical temperature gradient becomes steeper than the adiabatic, convection currents will be set up. These currents will transfer heat so readily from the bottom to the top of the layer that we are entitled to assume, with Dr. Jeffreys, that they will effectively prevent any appreciable increase in the temperature gradient above the adiabatic value.

If this adiabatic temperature gradient were steeper than the rate of rise of melting-point with depth, then the liquid at the top of the layer might be at its melting-point, and so in equilibrium with the solid roof ; but if the melting-point gradient is the steeper of the two, then, since the deeper parts cannot be below their melting-point, the upper layers must be above their melting-point, and so the roof must melt. This was pointed out many years ago by Lord Kelvin, who, however, had not the necessary data to decide whether the "ice line" for basalt is more or less steep than the adiabatic for liquid basalt. He showed that if, as he expected, the "ice line" were the steeper, then a column of basalt cooled at the top would solidify at the bottom, but the reverse would hold if the adiabatic were the steeper. Our knowledge of the required data is a little more complete, and enables us to form some quantitative idea of the two gradients in question.

The adiabatic gradient is given at once from the well-known formula,

$$\left(\frac{\partial \tau}{\partial p}\right)_{\phi} = \left(\frac{\partial v}{\partial \phi}\right)_{p},$$

where τ, ϕ, p, and v represent the absolute temperature,

entropy, pressure, and volume, respectively, of a given mass of any substance, and the suffixes indicate the constancy of the quantity named. Substituting for the right-hand side, we get

$$\left(\frac{\partial\tau}{\partial p}\right)_{\phi} = \frac{\tau\alpha}{\sigma\rho},$$

where α is the coefficient of cubical expansion and σ the specific heat (in work units), both at constant pressure, and ρ is the density.

If x is the depth measured from any origin, we have, since $\frac{dp}{dx} = g\rho$,

$$\left(\frac{\partial\tau}{\partial x}\right)_{\phi} = \frac{\tau\alpha g}{\sigma}.$$

τ may be taken as 1200° C., *i. e.* 1473° absolute.

From Day, Sosman, and Hostetter's * work we find that, at atmospheric pressure, α for liquid basalt is about $6{\cdot}5 \times 10^{-5}$. Some allowance for the effect of pressure might be made from the relation $-\left(\frac{\partial\alpha}{\partial p}\right)_{\theta} = \left(\frac{\partial \mathrm{C}}{\partial\theta}\right)_{p}$, where C is the compressibility, if we knew the value of $\left(\frac{\partial \mathrm{C}}{\partial\theta}\right)_{p}$ for liquid basalt. This is unknown, but is almost certain to be positive, so that α, and hence the adiabatic gradient, will decrease with increase of depth. g may be taken as 981 cm. (per sec.)^2.

As regards σ, the value that we should expect for solid basalt at sufficiently high temperature, as calculated from its composition, is about 0·28. This accords perfectly with some measurements made by one of us †, which gave values rising at a decreasing rate from 0·20 at 50° C. to 0·26 at 600° C. The specific heat of a substance always being greatest in the liquid state, it would seem that the specific heat of liquid basalt must be at least 0·30, or when reduced to work units, $1{\cdot}25 \times 10^7$.

Putting in these values, we find that the adiabatic temperature gradient comes out at 0·75° per kilometre, at the surface, decreasing with increase in depth.

The melting-point gradient is, of course, found from the equation

$$\frac{d\mathrm{T}}{dp} = \frac{\mathrm{T}(v_2 - v_1)}{\mathrm{L}},$$

where T is the melting-point (absolute), L the latent heat

* Amer. J. Sc., January 1914.

† Phil. Mag., January 1914.

of fusion in work units, and v_2 and v_1 the specific volumes of the liquid and solid magma respectively.

Hence, as before, since $\rho = \frac{1}{v_2}$,

$$\frac{dT}{dx} = \frac{gT}{L}\left(1 - \frac{v_1}{v_2}\right),$$

T may be taken as identical with τ, *i. e.* 1473°, and L as $90 \times 4{\cdot}2 \times 10^7 = 3{\cdot}8 \times 10^9$ work units.

To find $\frac{v_1}{v_2}$ we have Day, Sosman, and Hostetter's result that solid basalt expands 10 per cent. on melting at air-pressure. On the other hand, allowance must be made for the different compressibilities of the solid and the liquid. Adams and Williamson * have shown that, up to pressures of about 12,000 megabars (corresponding to a depth of about 40 kilometres), C for solid gabbro is about $1{\cdot}2 \times 10^{-6}$ per megabar, and is very nearly independent of the pressure. These experiments were made at air temperature, but the good agreement between the velocities of earthquake waves calculated from them and those found for moderate depths indicates that the effect of temperature is small.

Very few measurements are available on the effect of liquefaction on the compressibility of substances. Richards, Bartlett, and Hodge † found $30{\cdot}5 \times 10^{-6}$ and 72×10^{-6} as the values of C for solid and liquid benzene, respectively, showing that melting increased the compressibility about 2·4 times. On the other hand, liquids always show a decrease of compressibility with increase of pressure. Thus Adams, Williamson, and Johnston ‡ found that the mean compressibility of kerosine oil fell from 27×10^{-6} for a pressure range 2000–3000 megabars to 15×10^{-6} for a range 2000–12,000 megabars, the value for the range 11,000 to 12,000 being only 8×10^{-6}.

Thus it would seem to be very unlikely that, at the pressure involved, the compressibility of liquid basalt would be greater than twice that of the solid, *i. e.* $2{\cdot}4 \times 10^{-6}$.

This would have the effect of reducing v_1 by 1·44 per cent., and v_2 by 2·88 per cent. at 12,000 megabars pressure, so that the expansion on melting would be reduced to 8·56 per cent. Thus, at a depth of 40 kilometres, $1 - \frac{v_1}{v_2}$ would be 0·079. This would make $\frac{dT}{dx} = 3{\cdot}0°$ per kilometre.

* J. Franklin Inst., April 1923.
† J. Amer. Chem. Society, July 1921.
‡ J. Amer. Chem. Society, January 1919.

Thus the melting-point gradient comes out as 4 times as steep as the adiabatic at a depth of 40 kilometres. It will be noticed that the effect of the compressibilities, assumed above, is to reduce the melting-point gradient by 14·4 per cent., no allowance being made for the effect on the adiabatic. To make the gradients equal at this level, we should have to assume a compressibility for the liquid nearly 6·5 times as great as that of the solid, and disregard the effect of this compressibility on the coefficient of expansion. With the above assumptions as to compressibilities, the gradients would become equal at a depth of about 220 kilometres.

It would therefore appear to be very improbable that, at depths less than 200 kilometres, the adiabatic could be steeper than the melting-point gradient. It is possible that at greater depths the adiabatic might be the steeper. Here, however, other materials would probably occur, and the pressures involved would be so far beyond those for which any data are available that speculation at present appears rather futile.

Let us consider a layer of basaltic magma of such a depth that thermal conduction through the solid cannot carry off the heat generated by radioactivity in the magma, and that rising from below, readily enough to prevent the deeper layers from rising above their melting-point. In course of time melting would occur, and as the lower parts of the melted layer could not be below their melting-point, the top of the layer would necessarily be above its melting-point. Thus it would constantly melt its way upwards through the overlying roof.

The liquid which had been cooled by contact with the roof, and that formed by the fusion of the roof, would be above their melting-point but below the temperature proper to their level, and would sink through the magma. As this liquid sank, it would, in spite of the rise due to adiabatic compression, always be at a lower temperature than its surroundings, until it might reach such a depth that partial solidification occurred. Thus, unless there were a source of heat below, and in, the magma layer sufficient to provide all the latent heat of the melted roof and that lost by conduction through the roof, this heat would be partly provided by the solidification of magma in the deeper layers.

At first the resolidification in the deeper layers might be small or entirely absent, and the liquid layer would increase in thickness at the expense of the overlying crust. As this became thinner the heat-loss through it would increase, and resolidification would set in in the deeper layers of the

magma. This would in time become equal to, and finally greater than, the rate of melting of the roof, so that the liquid layer would attain a maximum thickness, after which it would decrease again, while continuing all the time to eat its way upwards. It would finally disappear when it had risen to such a level that the loss of heat through the reduced crust caused complete solidification. The resolidified magma, underlying the liquid layer, would, as Lord Kelvin pointed out, be everywhere near its melting-point: thus at a depth of 40 kilometres the temperature gradient would be about 3° C. per kilometre, falling slowly with increase of depth. This gradient would only suffice to carry off by solid conduction the radioactive heat generated in a layer of basalt about 4 kilometres thick, or in one of eclogite or dunite 8 kilometres thick. Thus, remelting of the deeper layers would be inevitable, followed by repetition of the entire cycle.

Thus we seem to be driven to the conclusion that a deep layer of magma whose radioactivity is at all comparable with that of surface specimens of basic or ultra-basic rocks would undergo periodic changes of state, which would be accompanied by corresponding changes in the temperature gradient in the overlying crust.

The result would be quite independent of all assumptions as to the effects of tidal displacements, if the infusible continental masses were absent. Where, however, such granitic materials form an infusible crust of sufficient thickness, resolidification of the underlying basaltic magma would be prevented, so that the present solidity of the magma underlying the continents seems to be most readily explained by Dr. Joly's assumption that, during revolutionary periods, tidal effects in the liquid magma produce lateral displacements of the continental masses, and so allow the accumulated heat to escape.

We seem, then, to be faced with two alternatives :—

We may deny that the radioactivity of the deep-seated rocks is at all comparable to that of the specimens which are available to us. We must then either deny the occurrence of the revolutions that geologists have found such strong evidence for, or accept them as unexplained facts.

We may, on the other hand, assume that the radioactive measurements of available specimens are of some value. We then have an explanation of these revolutions forced upon us.

Royal Dublin Society,
January 5, 1928.

LXIX. *The Absolute Zero of the Externally Controllable Entropy and Internal Energy of a Substance and a Mixture.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper that appeared in the April number of the Phil. Mag. (1927) I showed that the controllable internal energy and entropy are zero of a substance under its vapour-pressure at the absolute zero of temperature, by means of the theorem, established in a certain way, that the specific heat at constant volume is a positive quantity. I would like to point out that this theorem can be shown to follow simply from our notions of heat as follows :—Suppose that a substance A is completely surrounded by a substance B at the same temperature, and that the former substance has a negative specific heat. Now suppose that the substance B is raised in temperature by ∂T. An initial flow of heat from B to A will take place; otherwise there would be nothing to indicate to the substance A that the temperature of the substance B has been raised by ∂T. An evolution of heat in the substance A will now take place, tending to produce a flow of heat in the opposite direction since its specific heat is negative. But suppose that this flow of heat is checked by keeping the substance B at the same temperature as that of the substance A till no further change in its temperature takes place. In this manner the temperature of the substance A may be raised to any value we please by repeating the process the necessary number of times. The substance A will evidently only receive heat under these conditions—in other words, a negative specific heat is impossible. The result will evidently hold whether the substance A is kept at constant volume or at constant pressure.

Yours faithfully,

R. D. KLEEMAN.

LXX. *Notices respecting New Books.*

Ordinary Differential Equations. By E. L. INCE, Professor of Pure Mathematics in the Egyptian University. Pp. viii+558, with 18 figures. (London: Longmans, Green & Co. 1927. Price 36*s*. net.)

THE subject of differential equations is one that has of recent years been seriously neglected in England. The reason for this, in the words of the author, is that "England has but one

school of Pure Mathematics, which implies a high development in certain fields and a comparative neglect of others. To spread the energies of this school over the whole domain of Pure Mathematics would be to scatter and weaken its forces; consequently its interests, which were at no time particularly devoted to the subject of Differential Equations, have now turned more definitely into other channels, and that subject is denied the cultivation which its importance deserves."

The standard English work on the subject, the 'Theory of Differential Equations,' by Professor Forsyth, is too comprehensive for the ordinary student, and now requires to be brought up to date, as there has been much work done in this subject since its publication. There was thus need for a treatise such as the one under review.

The treatise is not intended for the elementary student or for the student of physics or engineering, whose aim is merely to derive solutions of the equations which present themselves in the course of their work. It is written for the advanced student of pure mathematics, and demands of the reader a fairly comprehensive knowledge of modern analysis.

The volume is divided into two parts which deal with differential equations in the real and complex domains respectively. The appendices include a historical note on formal methods of integration and a note on the numerical integration of ordinary differential equations. References to original papers are given throughout.

The treatment is throughout clear and logical, and no serious errors have been noted, though there are a number of misprints—generally obvious—which are accounted for by the fact that, owing to his appointment at the Egyptian University, the author was unable to correct the final proofs.

Professor Ince is to be congratulated on having written a treatise which will undoubtedly be found of very great value by the students of pure mathematics and which, it may be hoped, will do something towards stimulating the study of differential equations in England.

An Outline of Stellar Astronomy. By Peter Doig, F.R.A.S. Pp. viii + 183, with 24 figures. (London: Draughtsman Publishing Co. 1927. Price 7*s.* 6*d.*, post free.)

Mr. Doig writes in a very lucid manner of some of the modern developments of stellar astronomy, and the student who from lack of mathematical equipment is unable to appreciate many of the original papers will find this little volume a great help. Even the more advanced student will find it of interest, for the author brings an original mind to bear upon the subject.

The volume is not suitable for a first introduction to stellar astronomy. It is not sufficiently connected or comprehensive. It consists to all intents and purposes of a series of notes which illuminate different aspects of the subject. An extensive field is covered; the observational data are first dealt with—the dimensions, luminosities, and masses of the stars; their numbers, movements, and distribution; binary and variable stars. Modern views as to the nature of a star and the cause of stellar evolution are summarised. Finally, the structure of the galactic system and of external systems—the Magellanic Clouds, spiral nebulæ, etc.—is discussed.

There are numerous diagrams and reproductions of astronomical photographs, but the latter are in general of poor quality.

LXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 224.]

November 30th, 1927.—Dr. F. A. Bather, M.A., F.R.S., President, in the Chair.

Prof. D. I. Mushketov, Director of the Russian Geological Survey, gave a brief account, illustrated by lantern-slides, of the results of recent work in the Alai and Trans-Alai chains in Southern Turkestan, north of the Pamirs. The first geological survey of this region was made in 1909. The results then obtained have been confirmed and amplified by the surveys of 1925 and the two succeeding years made by the speaker and by A. P. Markovski. In the western part of the Alai chain abundant confirmatory evidence was obtained of a Pamir (Alpine) system of folding, due to pressure from the south acting in Kainozoic times and causing overthrusting of Palæozoic rocks over Cretaceous and Tertiary. Observations in the western part of the Trans-Alai chain lead to the conclusion that the northern slope of this part of the chain is a large isosyncline, overturned northwards and lying nearly horizontal. Its core consists of much-folded Upper Cretaceous and Eocene marls and clays, raised by the folding to a height of some 18,000 feet. It seems likely that the whole of the Trans-Alai chain was overthrust on to the Alai chain to the north.

East of the meridian of Mount Kaufmann the direction of the whole Alai chain swings from an east-to-west to a north-to-south direction—the 'Ferghana flexure.' On the southern limb of this flexure there has occurred another great overthrust, a sheet of massive Devonian limestones having been thrust from south to

north over Kainozoic and Cretaceous beds. The surface of this over-riding sheet dips distinctly south-eastwards at 35°. The observations of the recent Pamir expedition under D. V. Nalivkin confirm the views arrived at in the Alai chains.

The following communication was read :—

'The Granites of the Scilly Isles, and their Relation to the Dartmoor Granites.' By Charles William Osman, M.Inst.C.E., F.G.S.

Assuming that the whole of the granites of Devon and Cornwall are due to the same cause, late adjustments of the post-Carboniferous revolution, it is shown, by comparing the two ends of the series, that the isostatic correction-sequence of intrusions is similar in both areas.

The separate successive intrusions are tabulated for both areas in their corresponding stages.

Previous to the intrusion of the granites the South-West of England had been subjected to three separate foldings, and the positions of the granite-laccolites are directly related to the intersection of the ridges of these folds: (*a*) Post-Silurian, Caledonian folding; (*b*) Post-Middle Coal-Measures, Malvernian folding; and (*c*) Post-Carboniferous, Armorican folding.

Although the order of the granitic intrusions is found to be the same throughout the whole district, it would not appear that all these took place simultaneously, and reasons are given to show that the Scilly Isles and Bodmin-Moor Stage 2 A granites were intruded earlier, and had consolidated before the Dartmoor Stage 2 A was intruded.

The Scilly Isles being a typical granite-laccolite that has been dissected by Nature, afford exceptional advantages for the study of the formation of such compound intrusions, having been planed down by the advance and retreat of the seas of the Upper Cretaceous Period, the Eocene uplift, and the Pliocene sea—so that now no part rises higher than 166 feet above mean sea-level. Also numerous cross-sections have been made by the formation of north-south sea-channels, probably due to slight further Malvernian movement.

Stage 1 is a basic microgranite found only as inclusions in Stage 2 A coarse-grained, and Stage 2 B medium-grained granites.

The directions of flow of the granite for Stages 2 A & 2 B are traced back to their inlet. Stage 3 is a fine-grained granite, intruded after the previous stages had consolidated, and it is shown that Stage 3 not only made a new inlet, but, in doing this, formed thrust-planes of low hade in Stage 2 A and Stage 2 B intrusions. The later subsidence of the inlets produced Crow Sound and St. Mary's Sound, and the age of these inlet subsidences are possibly as late as the Pneumatolytic Stage. Stage 4 is a later fairly large marginal intrusion of a microgranite of

aplitic nature, intruded locally between Stage 2 B above and Stage 3 beneath. All these stages in Scilly entered the laccolite from the two inlets mentioned.

The secondary smaller intrusions of aplites have dyke sources principally along Caledonian direction-faults, and form sill-intrusions into shrinkage and other joints.

The Pneumatolytic Stage is represented by greisen lines and schorl-quartz reefs, which generally infill small faults of Caledonian trend.

The principles of the granite-magma crystallization shrinkage-jointing are described in regard to the production of pseudo-anticlines and synclines, as being significant of direct roof-cooling influence, and the effect of roof-subsidence during the consolidation of such structures is dealt with and examples are given. It is also shown that the deeper into the laccolite the jointing is observed the flatter the bed-joints become, as the roof-cooling influence is exhausted, until in the centre of the islands the bedding-joints are horizontal.

The later faulting and bands of slip-shearing in the granites are considered, and the effect on the present features of the Scilly Isles is described.

Petrological details are given to show the distinct differences between the granites of Bodmin Moor and the Scilly Isles and the remainder of the South-Western granites, indicating a different source; and it is suggested that these two granite-laccolites were supplied from a great Caledonian direction-fault or series of faults parallel with, but some miles off, the north-western coast of Cornwall; also that only from such great faults could the allied Lundy-Island granite have been intruded, all the other granite-laccolites being intruded from the Start-Lizard series of faults.

The pre-granitic xenolithic inclusions in the Scilly granites indicate a great difference in age between the floor and the roof of this laccolite. The contorted schist inclusions are similar to the biotite-felspar-andalusite-garnet-schists of the south-west of the Lizard. These may be Archæan, or possibly of Lower Palæozoic (Mylor) age, and the granites probably rest on a platform of similar rocks; while the uncontorted quartz-biotite-cordierite-spinel-schists, though possibly of Devonian age, so closely resemble the Lower Carboniferous inclusions of Dartmoor, that those rocks probably formed the roof of this laccolite.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]